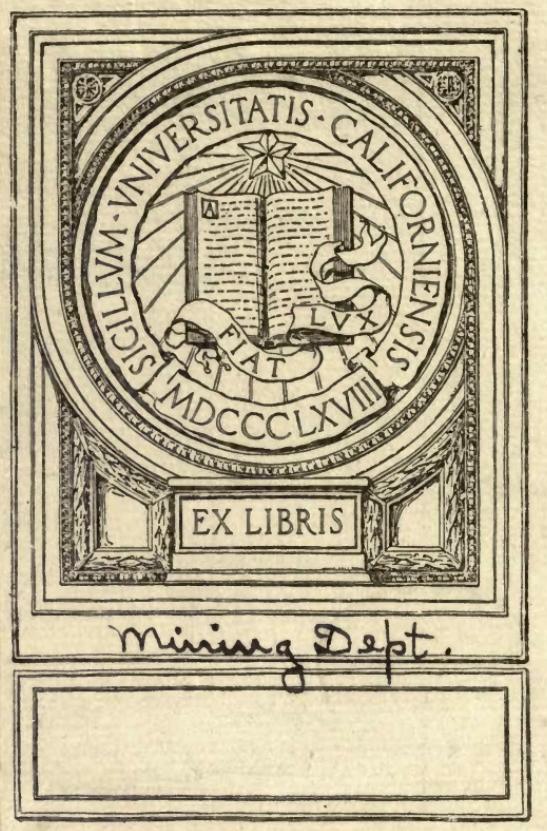


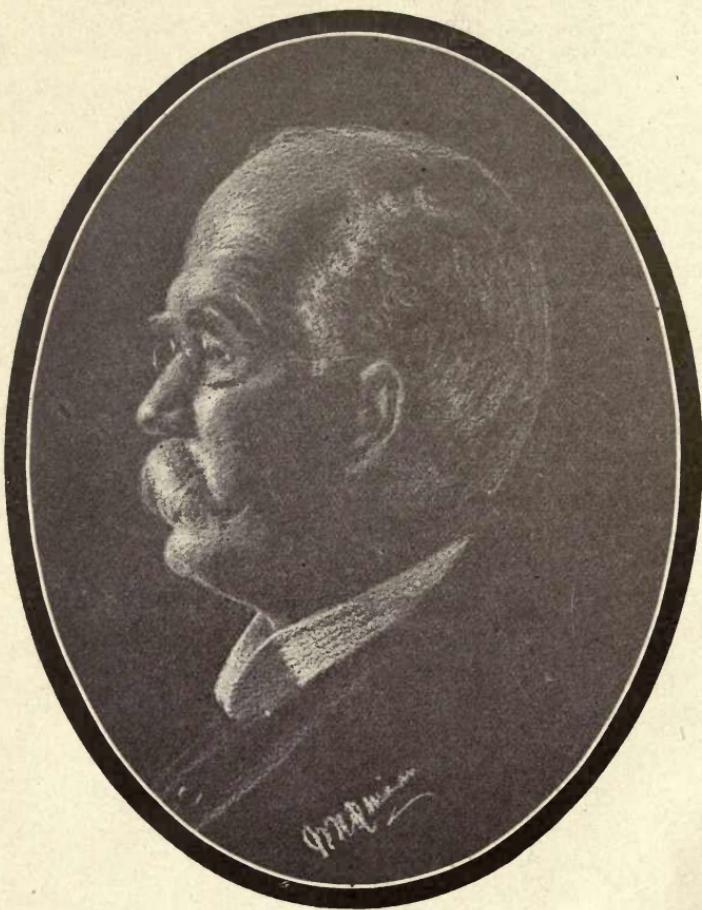
UC-NRLF



B 3 112 978







THE AUTHOR.

HIGH EXPLOSIVES

BY

W. R. QUINAN.
II



21/- NETT

LONDON
SIR ISAAC PITMAN & SONS, LTD., 1 AMEN CORNER, E.C.
BATH AND NEW YORK.

1912.

TP 270

Q 7

MINING DEPT.

Mining Dept.

Copyright, 1912,
by
Critchley Parker.

THE MINE
AUDITORIALS

Printed in Australia.

INTRODUCTION.

By T. J. WRAMPELMEIER.

The concluding chapters of this book were written while the author was in the last stages of a severe illness, to which he succumbed on August 15th, 1910, at Wahroonga, New South Wales.

William Russell Quinan was born in Maryland, U.S.A., in 1848. He graduated from West Point, the Military Academy of the United States, in 1870, having distinguished himself for proficiency in mathematics and the physical sciences. After some years' service in the artillery, he resigned his commission in 1881 to devote himself to the development and manufacture of industrial explosives. His first engagement was with the California Vigorit Powder Company. From 1883 until 1899 he was Superintendent of the California Powder Works. In 1899 he was engaged by the late Cecil Rhodes to build a dynamite factory in South Africa, and was appointed General Manager of the Cape Explosives Works, Limited. He remained with this company until the end, and it was while in Australia in its interest that the last illness overtook him.

As member of a number of scientific societies, he was an occasional contributor to the journals, but his active duties did not leave him much time to write for publication—his best work being done in his official reports to his Directors. He was prolific as an inventor, though most of his inventions were not patented. Among the most important of his inventions relating to the explosives industry were the Crusher Gauge for testing high explosives, the Quinan Packing Machine (the first successful machine for packing dynamite into cartridges), improvements in the manufacture of sulphuric acid, and numerous explosive compositions.

Quinan was distinguished, not only for his scientific attainments, but for his integrity of character, his loyal friendship and his loving characteristics as husband and father.

CONTENTS.

CHAPTER I.

HISTORICAL.

Alfred Nobel.—Detonation.—Vagaries of Nitro-Glycerin	1-11
--	------

CHAPTER II.

VELOCITY OF DETONATION.

Dr. Comey's Determinations.—Use of the Detonating Fuse. (This chapter is devoted to giving a summary of a very interesting paper by Dr. Arthur M. Comey, Director of the Laboratory of the Dupont Powder Company of America, entitled, "Study of the Velocity of Detonation.")	12-19
--	-------

CHAPTER III.

INDUSTRIAL EXPLOSIVES.

Nobel's Dynamite.—Modern Dynamites.—Gelatinous Explosions. — Freezing. — Sensitiveness. — The "Hake Effect."	20-29
--	-------

CHAPTER IV.

AUSTRALIAN CONDITIONS.

Exudation of Gelatins.—Tests for Sensitiveness.—Open Tests	30-36
--	-------

CHAPTER V.

THEORY OF EXPLOSIVE ENERGY.

Energy of Explosives.—Uncertainties of Science.—Theory of Explosive Energy.—The Chemical Equation of Metamorphosis.—Dissociation and Lack of Reliable Scale for High Temperatures	37-48
---	-------

CHAPTER VI.

AVAILABLE ENERGY OR MAXIMUM WORK.

The Available Energy of an Explosive.—Diagram for Nitro-glycerin. — Tables. — Available Energy as Affected by Dissociation.—Diagram for Nitro-glycerin	49-66
--	-------

CHAPTER VII.

USEFUL WORK.

Useful Work.—General Principle for Hard Rock.—Bank Blasting.—Classification of Explosives.—Tests for Energy.—Mortar.—Quinan Crusher Gauge.—Work in the Mortar.—Effect of Dissociation.—Effect of Rates of Detonation	67-83
--	-------

CONTENTS.

CHAPTER VIII.

STRENGTH OF EXPLOSIVES.

Tests for Strength.—Density of Loading.—Pressure of Gunpowder.—Rumford, Piobert, Rodman, Nobel and Abel.—Pressure of High Explosives.—Berthelot, Sarran and Vicille.—Testing Devices.—Guttmann's Pressure Gauge.—Trauzl Lead Block.—Bichel's Pressure Gauge

84-98

CHAPTER IX.

THEORIES OF EXPLOSION.

Limitation of Theory.—Vortex Action.—Direction of Maximum Action.—Behaviour of Guncotton.—Influence of Detonator.—Anomalies.—Pressure vs. Dynamic Effect.—Effect of Inequality of Action.—Case of Closed Vessels.—Velocities of Molecules.—High Densities of Charge.—Low Densities of Charge.—Bichel's Results.—Emmens' Ballistic Theory.—Sarran's Theory.—Bichel's "Percussive Force."

99-119

CHAPTER X.

DISSOCIATION.

Review of Practical Tests.—Disagreement with Theory.—Dissociation the Explanation.—Objections to the Accepted View.—Author's Dissociation Hypothesis.—Normal Dissociation.—Heat of Formation.—Work of Dissociation.—General Formulas for Dissociation.—Oxy-hydrogen Flame . . 120-144

CHAPTER XI.

DETONATION OF GASEOUS MIXTURES.

Detonating Gaseous Mixtures.—Views of Berthelot.—Formulas for Dissociation in a Mixture of Gases.—Detonation of Hydrogen and Oxygen.—Of Hydrogen, Oxygen and Nitrogen.—Hydrogen and Chlorine.—Carbonic Oxide and Oxygen.—Table of Detonating Gaseous Mixtures

145-178

CHAPTER XII.

DISSOCIATION OF EXPLOSIVES.—SPECIFIC HEATS.—

BOYLE'S LAW AT HIGH DENSITIES.

Dissociation in Explosion Products.—Nitroglycerine as Illustrations.—General Principles.—Estimates of Dissociation in N.G. Products.—Mercury Fulminate.—Dissociation of its Products.—Question of Specific Heats.—Not Increased at Explosion Temperature.—Boyle's Law at High Densities.—Isothermals of a Perfect Gas.—Isothermals of an Imperfect Gas.—Isothermals of Hydrogen.—Improvement with Temperature.—Increase of Pv at High Densities.—Experimental Evidence.—Pressures of Explosives at Absolute Densities

179-208

CHAPTER I.

Historical.

Alfred Nobel.—Detonation.—Vagaries of Nitro-Glycerin.

Alfred Nobel—From this year, A.D., 1910, the introduction of high explosives into the engineering industries dates back about half-a-century. The world owes this great boon mainly to the genius, or to be more critical, to the iron courage and perseverance of one man—Alfred Nobel, the Swedish engineer. It was he who tamed nitro-glycerin and subdued it to the hand of the miner. Nitro-glycerin had been discovered 10 or 12 years before Nobel began the work of studying it, learning its nature and properties, and turning these to practical account. Little was known about it, except that it had wrecked a number of laboratories in different parts of Europe, where chemists had attempted to follow up Sobrero's discovery. The story runs that his father Emmanuel Nobel, who had moved to St. Petersburg, and was a dabbler in explosives, was employed with a Professor Jacobi in devising a system of submarine torpedoes for the Russian Government during the Crimean War, to keep the Allied fleet out of the Neva. It is probable that the elder Nobel thus learned how to make nitro-glycerin on the small scale practised by chemists. Some time after the war he returned to Stockholm and put up a tiny factory for its manufacture. This was in the later fifties—probably in 1859. Alfred Nobel, who had returned a year or two before from an apprenticeship in America, became interested in the enterprise, and put his shoulder to the wheel. An explosion at the little factory killed his youngest brother Johannes, and broke the father's heart, but even this could not daunt Alfred Nobel. He had grasped the significance to the industrial world of this new agent—nitro-glycerin—and nothing could turn him back. He found funds to build a new factory, and devised apparatus for manufacturing it on a large scale—apparatus that has been

copied with slight modification by all manufacturers of modern date. He sent out nitro-glycerin packed in bottles or tin cans to various parts of the world, under the trade name of "glonion oil." In nearly every instance he received news sooner or later from each consignment of a disastrous explosion.

To mention some of these:—There was one on a steamer lying at Aspinwall, on the Isthmus of Panama; a ship going to Chili was blown up; there was an explosion at Quenast, in Wales; another in a New York Hotel; and still another in Wells, Fargo's Express office in San Francisco. This latter explosion was caused by part of a lot consigned to Julius Bandmann, to whom Nobel afterwards assigned the United States patent for dynamite taken out in 1867. What iron nerves the man must have had! The terrible news arriving in instalments distressed him, but he never wavered from his purpose. He went on patiently with his experiments. He had solved the problem of making nitro-glycerin on a commercial scale, but two other problems pressed. One was to prevent it from exploding when an explosion was not wanted—the other was to explode it when an explosion was wanted. Nobel was not by training a chemist, and did not at first realise the necessity of thorough purification of the nitro-glycerin. The disasters referred to were generally the result of slow decomposition of the nitro-glycerin under confinement. During a certain stage the decomposing liquid is very sensitive to jar or shock, while it generally explodes spontaneously some time or other if kept bottled up. The pioneer, in clearing up this matter, though his work came some years later, was Geo. M. Mowbray, who manufactured liquid nitro-glycerin for boring the great Hoosac Tunnel, at North Adams, Massachusetts. Mowbray, who was a chemist, saw at once that it was necessary to thoroughly purify the nitro-glycerin by washing out all traces of the acids to prevent decomposition. He set a standard in this regard which all later manufacturers have been glad to follow. It remained, however, for Nobel to strike the keynote of safety. It was he who first clearly realised that the liquid form of nitro-glycerin was in itself a danger. Liquids being incompressible, are ill-

suited to withstand the shocks and jars of transportation and use when they are explosive. Hence came the invention of dynamite. By absorbing nitro-glycerin in a porous earth called Kieselguhr, he obtained an explosive paste with some resilience and capacity for absorbing shocks. This was "dynamite," or Nobel's safety powder—the greatest practical step in high explosives.

Going back to the other problem—getting the nitro-glycerin to explode when the bore hole was charged and everything was ready for the blast—Nobel must have been surprised when he found his servant capricious and baulky in the extreme. His earliest patents show that he expected to overcome the difficulty with gunpowder. By exploding this in the bore hole he anticipated setting free the great energy of the nitro-glycerin, but it was no go. Sometimes he got an explosion of a low order, and sometimes a total failure. He even mixed the two together, but this worked even worse. The mixture burnt without developing even the useful energy of gunpowder. Finally, he hit upon the idea of using gun caps charged with mercury fulminate. He was on the right track at last, and when he lengthened the copper tubes and used comparatively heavy charges of fulminate composition the problem was solved. Detonation of a high explosive at will made its appearance for the first time; success was reached in 1864. This, one of the most important and far-reaching of his inventions, was not patented.

By 1867 Nobel had overcome all the tremendous difficulties in his path, and given the world a working high explosive—dynamite—which served its purpose well for nearly twenty years.

Before saying good-bye to this wonderful man I wish to recapitulate that he was the first to solve the problem of making nitro-glycerin on the large scale, to devise a means for detonating it, and to invent a safe form for its use. In subsequent years he patented blasting gelatin and ballistite, both record-making inventions. The first remains the most powerful, and the ideal explosive for the miner where great energy is required, while the second was the forerunner of smokeless

powder, containing nitro-glycerin as an ingredient. Cordite is an offshoot, so to speak, of this invention.

Alfred Nobel may be called the Father of High Explosives. Simple in character, and practical in his work, his fame should be cherished among those who are engaged in the making and handling of modern industrial explosives. In the dark days, when little was known of the nature of the terrible agent, nitro-glycerin, it was he who had the courage to drag the monster into the light, and chain him to be the obedient servant of man. He had to grope his way and learn by bitter experience, but when once started upon his task, like Christian, in Bunyan's "Pilgrim's Progress," he set his teeth and moved always forward. As an humble follower in his footsteps, I take great pleasure in making this simple tribute to his memory.

Detonation.—Every one knows that there are two forms of explosion—combustion and detonation—and the average man's idea of the two phenomena is fairly definite; but few know that there are intermediate forms or lower orders of detonation—explosions which it is impossible to accurately classify. Various theories have been proposed for detonation. The one generally accepted is the wave theory. According to this, the detonator sets up a wave of short but intense vibrations, which, radiating from it, cause the successive layers of the explosive to undergo a sudden chemical transformation. The wave is reinforced by the successive explosions and carried onward to the bounding surfaces of the stuff with a high but definite velocity, which is determined by the nature of the explosive, and the special conditions of the experiment. One might think that whatever the initial order of the explosion, the great energy set free in the successive layers would determine the final velocity of detonation; that is, if the column of explosive were long enough, the velocity would attain a certain normal figure, no matter how the wave was started, whether by a weak or strong detonator, but under the conditions of use this is certainly not so. A weak wave remains weak and retains a low velocity. This fact alone, notwithstanding the complication of the phenomena involved, tends to show that a true wave is concerned, the velocity of which, in a given explosive

medium, is mainly dependent upon the intensity of its vibrations.

Mercury fulminate, so far as is known, is the detonating agent par excellence. Berthelot, the great French authority, holds that of all known explosives, it is capable of producing the greatest pressure on the unit of confining surface. He ascribes this to two of its properties—first, to the simplicity of its chemical metamorphosis, which gives non-dissociable products, one mercury vapour being monatomic and the others diatomic*; second, to its great density, which enables one to concentrate its action, and apply it to a small area. It is also known to have a very high velocity of detonation—probably the highest of any known explosive, except, perhaps, some of the other fulminates. It is readily exploded by friction, shock, spark or flame. Whether it undergoes combustion or detonation by simple ignition depends upon the confinement. Small quantities unconfined burn up with less violence than fine gunpowder under the same conditions. It must be noted that the energy of mercury fulminate is very small, and its effects local. Theoretically, energy is independent of quickness. It is a question of heat and gas volume.

When Nobel found that he could produce the detonation of nitro-glycerin by using a copper capsule charged with fulminate, the idea spread rapidly to all parts of the world where nitro-glycerin or its preparations were used, and in a few years dynamite caps were articles of commerce. The Germans were prompt to take up the manufacture as well as the factories in New England which had been engaged in making cartridge cases and caps for guns. These early dynamite caps were woefully inadequate. They were short copper tubes, scarcely half an inch long, containing only a few grains—rarely more than three—not of fulminate, but of fulminate composition. Parenthetically, it may be said that the handling of pure fulminate is so dangerous that the cap manufacturers

*It will be seen later that, according to my view, diatomic molecules are subject to dissociation, but less so than molecules of greater complexity.

usually mix a diluent with it to lessen the risk of accident to the workmen. This diluent is generally potassium chlorate, and a composition in vogue in England and on the continent is 80 per cent. fulminate to 20 per cent. chlorate. Some makers use the proportions 95 to 5. A small percentage of guncotton has also been used; also of other explosives, nitro-saccharose and nitro-mannite. It is a point well worth determining whether any of these additions are really helpful to the detonation. They increase the energy, but it is not known how they affect the efficiency of the detonator in setting up the right sort of vibration. The right sort of vibration may also vary with the nature of the explosive. It is to be hoped that before long some skilled experimentalist will take up this study and make the subject clear. The cap factories could perhaps tell us something, but they keep their knowledge to themselves. The ordinary tests for caps, except for comparing the strength of those of like composition, being energy tests, are fallacious.

It is well to note here that the detonation of dynamite caps is obtained by simple ignition under confinement. In the ones made to fit safety fuse, the fuse supplies the ignition as well as the confinement. In the electric detonators there is a sensitive priming composition set on fire by the current, either by a spark in high tension fuses, or by the tiny red-hot platinum wire forming the "bridge" in low-tension fuses. Good confinement is necessary in both cases to develop the detonating power of the fulminate. Especial care should be taken in preparing detonators for firing with safety fuse, otherwise the detonation of the "charge" may be crippled at the fountain head.

The history of the introduction of detonators and detonating explosives on the mining fields repeats itself all over the world. It took years to root out the notion that "any little old thing" in the way of a detonator was good enough to explode dynamite. My experience in the Pacific States of America, where I began the manufacture of industrial explosives thirty years ago, will be found typical. The market was flooded with the tiny detonators mentioned above, called "single force" caps.

There were better ones—double and triple force—but they were scarce and hard to obtain. Some years later the two lower grades had disappeared. A local factory was established, and a quadruple and quintuple cap were made. The latter, if my memory serves me, contained about 12 grains of composition. This was a great improvement, but it took something like ten years of constant agitation by a few progressive spirits to reach even this stage. Truly, the miner underground has been long-suffering. In the early days of high explosives he must have accepted the rapid pulse and violent headache of his calling as a necessary accompaniment to the use of dynamite, whereas these distressing symptoms were chiefly due to the vapour of unexploded nitro-glycerin thrown into the air of the drive after every blast. Mowbray, at the Hoosac tunnel, noticed this effect when weak caps were used with his liquid nitro-glycerin, and a similar state of things prevailed for many years afterwards in the use of the various forms of dynamite. Kieselguhr dynamite, as well known, when properly detonated produces no bad gases, but in practice this was only on a par with badly proportioned dynamites having active bases. In fact, this was the period of bad dynamites. Some were worse than others, but all were bad, because with the weak caps in vogue they could not be properly detonated. It was not until strong caps were introduced that it became worth while for the dynamite maker to study compositions.

Vagaries of Nitro-glycerin.—The experiments of Dr. Comey, of the Dupont works, in America, are the latest observations on the detonation of high explosives. A summary of his paper is given in the next chapter. This is well worth study, because, reading between the lines, one can learn a good deal about the laws governing detonation. Take nitro-glycerin, for instance, which is rightly regarded as the most dangerously sensitive explosive that the dynamite maker uses as a component. Yet even this explosive needs strong confinement and heavily charged caps to develop the highest rate of detonation. In glass tubes it virtually failed. Tubes of $\frac{1}{4}$ in. bore would not transmit the detonation; $\frac{3}{8}$ in. tubes gave a detonation, but

evidently a crippled one, since the velocity was only 654 metres a second. One-inch tubes of light sheet iron seemed to be on the border-line of the requisite confinement, because two widely different velocities of detonation were obtained with 24.5 grain caps. Strong 1½in. iron pipes, however, were required, with 24.5 grain caps, to give the maximum velocity of detonation, but even with this size of column of explosive and strong confinement, weak detonators (12.1 grains) gave low velocities. The most curious feature of this investigation is that nitro-glycerin appears to have two widely different velocities of detonation, with no intermediate steps. The low rate covers a range up to about 2000 metres, while the high rate, beginning at 3½ times this, extends to 8000 or 9000 metres.

The early experimenters, Professor Abel among them, trying to detonate a stream of nitro-glycerin in an open trough, got a low rate, about 3000 feet a second. Liquid nitro-glycerin, in fact, has been more or less of a puzzle to practical men. ~~confined in tin cans, regarded it as the quickest of all high velocity of detonation.~~ For instance, Mowbray, who knew the importance of strong detonators, and who used it in boreholes confined in tin cans, regarded it as the quickest of all high explosives; but as he was an enthusiast, and believed he was the only maker of tri-nitro-glycerin, while Nobel and others were making an inferior grade, his opinion does not now inspire much respect. On the other hand, General Abbot, of the United States Engineers, in his great work at the Engineer Torpedo School, Willett's Point, in devising a system of submarine mines, found a curious anomaly in its action. He tried various explosives to ascertain their suitability for torpedoes, and determined their intensity by firing charges in the centre of a steel ring suspended at different depths under water. The steel ring was equipped with pistons and lead plugs, arranged symmetrically around the charge to record its action. Nitro-glycerin was fired in tin cans. He found that it gave only about eight-tenths of the intensity of Kieselguhr dynamite. Seeing that the dynamite contained only 75 per cent. of nitro-glycerin, the remainder of the composition being inert, this result seemed to show that a part was greater than

the whole. General Abbot, though sorely puzzled, verified the fact by numerous experiments. Influenced possibly by Mowbray's opinions, he offered as an explanation this theory—that the action of the nitro-glycerin might be too quick to be transmitted by the water surrounding the charge. As a practical maker of explosives, I was not satisfied with this explanation. I knew that nitro-glycerin, at least under certain conditions, was not quick, but slow. I took the trouble to construct a special crusher gauge (a modification of the Quinan gauge), in which the nitro-glycerin acted upon the lead plug through a column of water—that is, the blow from the explosive was partly transmitted by a column of water enclosed between water-tight pistons. The crushing of the lead plug gave the usual result as compared with the action of dynamite, the relative energy indicated being a little more than 100 to 75. In a paper published in the proceedings of the United States Naval Institute, No. 64, entitled, "Crusher and Cutter Gauges for Explosives," I gave an account of my experiments, and suggested that the explanation for the anomaly noticed by General Abbot in the behaviour of nitro-glycerin was that a considerable portion of it was not detonated, but escaped explosion by being blown into the surrounding water. In the light of Dr. Comey's experiments, I have no doubt that this was the true explanation. The confinement in the tin can with the detonator used was not sufficient to develop a high rate of detonation—the can was burst, and part of its contents scattered before the detonating wave reached the outer portions.

A curious observation made after an explosion at our factory, in California, receives some light from Dr. Comey's discovery that nitro-glycerin is subject to two widely different velocities of detonation apparently without intermediate steps. A decomposition of waste nitro-glycerin in a nitrating house started an explosion, which, following down a V gutter, carried the disaster to a mixing house, some 500 yards distant. The V gutter was made of two redwood boards, about 8 inches wide, rough on the outside, nailed together at the angle, and lined with light sheet rubber packing. At the time of the disaster

the gutter was carrying a stream of nitro-glycerin about $3\frac{1}{2}$ in. deep at the angle. The grade was about 14 in. in 100 ft. The gutter or flume was supported by wooden frames or horses of varying heights. At one point the gutter passed through the projecting toe of a hill, and to accommodate it a cut about 5 ft. in depth was made in a stiff, indurated clay, so solid that the walls of the cut were left nearly vertical. On one side of the gutter was a foot-walk for the cleaner, with the supporting trestle, hand-rail, and necessary framing. The other side was free, except for the legs of the horses carrying the gutter. In the cut on this free side the gutter was perhaps 18 or 20 inches from the clay wall. After the explosion the usual minute study was made of the ground. The V gutter was found wholly destroyed, and the frame knocked to pieces. The sheet-rubber packing was picked up in long strips, usually cut as with a knife along the line that had marked the level of the stream of nitro-glycerin. The curious observation referred to above was made in the clay cut, on the free side of the gutter. On the face of the clay wall was a perfect, nearly horizontal, imprint of the redwood board forming that side of the V gutter. A plaster cast could not have brought out the rough grain of the wood better. This imprint extended some 16 feet, showing that the board had been thrown intact horizontally against the clay wall, while nearly preserving the angle it occupied in the gutter, the imprint being much deeper in the upper part. Another strange thing was that the board had been utterly destroyed after making the imprint. Nothing remained of it but matchwood or shavings in the bottom of the cut, which reminded one of the floor in a busy barber's shop.

The natural conclusion was that the explosion could not have been instantaneous, even in the ordinary sense; that it either occurred gradually or in stages. With Dr. Comey's results to guide us, it is possible to propound a fairly simple explanation. Some small part of the nitro-glycerin stream (probably a small section at the angle, as being the part under the greatest confinement) detonated at the high rate, giving time for the board to be thrown against the clay bank and to make its imprint while it was yet intact, before the bulk of the liquid

detonated at the low rate and destroyed it. The explanation may seem far fetched, and if any better can be offered I will gladly accept it. It is hard to see how the flume could have been broken apart without scattering the liquid more or less, but we are dealing with very minute intervals of time, and this scattering would not necessarily prevent the subsequent explosion of all or the greater part of this nitro-glycerin. On the other hand, if the whole of the liquid in the gutter had been exploded as one body, the board would not have been "carried over horizontally to the clay bank; it would have been driven at an angle of 45deg. downwards, even if it had escaped immediate destruction, which is unbelievable. The other side of the cut, which was perhaps 3ft. or more from the gutter, showed no imprint, as though the board on that side had been overtaken and destroyed before it reached the bank.

CHAPTER II.

Velocity of Detonation.

Dr. Comey's Determinations.—Use of the Detonating Fuse. (This chapter is devoted to giving a summary of a very interesting paper by Dr. Arthur M. Comey, Director of the Laboratory of the Dupont Powder Company of America, entitled, "Study of the Velocity of Detonation.")

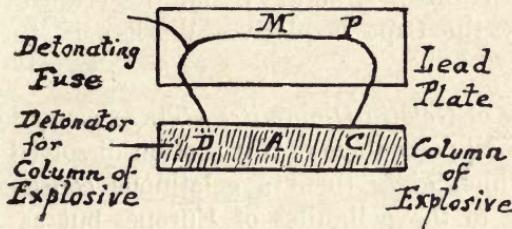
Dr. Comey's paper contains a detailed account of experimental determinations of the "Velocity of Detonation" in a variety of explosives, most of them peculiar to the American market, and differing from the European makes. Some of the results are very interesting.

The determinations were made by two methods—first, by the well-known Bichel method, in which a welded string of cartridges at least 10ft. long is detonated, and the time determined with an electrical chronoscope; second, by means of the new detonating fuse of M. d'Autriche.* This fuse, as used by Dr. Comey, is filled with a composition having a fixed velocity of detonation of 6000 metres per second. To make the experiment, a piece of fuse of suitable length is cut off, and the ends capped with detonators. The fuse is laid upon a heavy lead plate, and the middle point (M) of the fuse is marked upon the plate. If both caps are fired the detonating waves in the fuse meet at some point (P), and leave the plate indented in such a way that the point of meeting can be readily and sharply identified on the plate. If the caps are fired simultaneously the point of meeting of the waves is the middle point (M).

*This fuse is not the invention of M. d'Autriche, but he was the first to apply it in determining velocities of detonation, an account of which was published in *Comptes Rendus*. The fuse is the invention of M. Harle, of the *Poudres et Saltpêtres*.

To determine the velocity of detonation in a column of explosive, the terminal caps of the fuse are inserted in the column with a distance in metres (A) between them. The column is then detonated from one end. The meeting point of the waves in the detonating fuse is some point (P).

Let. $MP = b$, Let. X = velocity of detonation in the column of explosive.



T being the time it takes the waves to pass from D to P by the two paths DMP and DCP, we have:—

$$T = \frac{DMP}{6000} = \frac{A}{X} + \frac{CP}{6000}. \quad \text{DMP being equal to } CP +$$

2b, we have:—

$$X = \frac{6000 A}{2b}.$$

So delicate and accurate is the d'Autriche fuse in transmitting the detonating wave, that the ends of fuses can be inserted into the column of explosive at intervals of a few inches, and the velocity measured for these short spaces, and also the average velocity measured for the whole distance covered, in one experiment, so that an increase or decrease of velocity during the passage of the wave can be noted.

The first determinations were made with the Bichel apparatus. Some of the results were as follows:—

American Dynamites.—Various grades of American dynamites, that is, nitro-glycerin mixed with an active dope (nitrates and cellulose absorbents)—were tried—from 75 per cent. N.G. down to 5 per cent. N.G. It was found that the velocity diminished quite regularly with the grade from 6265 metres per second for 75 per cent., down to 1294 metres for the 5 per cent. Forty per cent. gave 4848 metres, 30 per cent. 4172, and 10 per cent. 2103 metres per second. The law of variation of the velocity in these “straight” dynamites (called “Lig-Dyns,” as made by the Cape Explosives Works) is therefore very simple.

Gelatins or Gelatin-Dynamites—These, as made in America, contain a small percentage of nitro-cotton dissolved in the nitro-glycerin, which gives them a gelatinous consistency, and a resemblance to the gelignites of Europe, but as a rule the Americans depend more upon the absorbent power of the cellulose ingredients, and use less nitro-cotton. The results were rather odd:—

Percentage strength	Velocity of Detonation—	
	Metres per second.	
75	2165	
60	2104	
55	2355	
50	2279	
45	2230	
40	2278	
35	2484	

In these tests gelatin-dynamite of the same grade was used as a primer, but caps of different strengths were employed without, however, causing any appreciable effect on the velocity. With the gelatins there is no increase in velocity, with increase in strength—in fact, a slight, but irregular, decrease is noted. But if a primer of 40 per cent. “straight dynamite” was used

to start the detonation, very different results were obtained, as follows:—

Gelatins with 40 per cent. Dynamite Primers.

Percentage strength		Velocity	of Detonation—
		Metres per second.	
75	6999	
60	6606	
50	5862	
40	5544	
35	5122	

showing not only a regular law of increase of velocity with the grade, but much higher velocities.

Ammonia Explosives.—These are dynamites in which part of the nitro-glycerin is replaced with ammonium nitrate. The following results were obtained, and were independent of the size of the detonator, or the use of a primer:—

Percentage strength		Velocity	of Detonation—
		Metres per second.	
60	3008	
50	4381	
40	4123	
35	3960	
30	3556	
25	3187	

These results are low, compared with the Lig.-Dyns. or "straight" dynamites, but high compared with the gelatins. The velocity for the 60-grade is anomalous. With this exception, there is an increase of velocity with the grade.

Nitro-Glycerin.—The plan of exploding this in glass tubes was first tried, but a tube with $\frac{1}{4}$ in. bore would not transmit the wave. The column could only be detonated for a few inches from the cap; $\frac{3}{8}$ in. glass tubes gave an average velocity using a 24.5 grain cap (1.6 grams) five tests were made. These of 654 metres per second. With 1 in. light sheet iron tubes, fell into two groups, one giving an average of 7690 metres, the

other only 1451 metres. With a 1½in. wrought-iron pipe, using a 24.5 grain cap, a velocity of 8527 metres was obtained, and with a cap containing 12.1 grains (0.8 grams) an average velocity of 2019 metres. (Using the d'Autriche fuse an average velocity of 7234 metres resulted.) We thus have the peculiar phenomenon with liquid nitro-glycerin of two widely differing velocities of detonation, with apparently no intermediate steps. The higher velocity evidently depends in a general way upon the size of the tube holding the liquid, the strength of the tube, and the use of heavy detonators. The results given so far were obtained by the method of Herr Bichel. They generally represent average velocities of detonation in welded columns of explosive 1¼in. in diameter and 10ft. long, enclosed in thin wrought-iron tubes. The d'Autriche detonating fuse was used specially to determine the law of increase or decrease in the velocity with the length of the column. The confinement was in a paper tube, and the average velocity obtained was therefore generally lower than by the Bichel method—strong confinement being favourable to higher velocities.

Tests with d'Autriche Detonating Fuse.—In these tests from one to four cartridges, 1¼in. x 8in., were generally used. The detonating fuses were used to determine the velocity of detonation in each stick or cartridge, as well as the average velocity for the whole column. Some of the results were as follows:—

gave an increasing velocity from 5066 in 1st stick to 5507 in 3

“Straight” Dynamites.—Sixty per cent. grade gave a 1
the 4th stick; 40 per cent. grade gave an increasing velocity 4
from 3901 in 1st stick to 4890 in 4th stick. This tendency 5
to increase reaches its maximum in the 40 per cent. The 6
nearly uniform velocity of 5800 metres; 50 per cent. grade 2
grades below 40 per cent. show the same tendency, but in 7
diminishing degree. The very low grades become nearly 8
uniform like the 60 per cent. 9

Gelatin-Dynamites.

	1st stick.	4th stick.
60 per cent.	2437 ..	2452
40 per cent.	2019 ..	2005

A single experiment, using a 40 per cent. "straight" dynamite primer on 60 per cent. gelatin, gave

1st stick.	3rd stick.
7304	6222

These results, though somewhat irregular, which was oftener the case with "gelatins" than with "straight" dynamites, show no particular tendency to increase of velocity with progression of the wave.

Blasting Gelatin.—A large number of tests were made with blasting gelatins, using 20 grain (1.3 grams) caps. It was found that the velocity of detonation increased very rapidly from a low velocity at the point of detonation, and reached a maximum in about 4 inches. Results of tests with a sample of blasting gelatin gave an average velocity of 2000 metres for the first 2 inches, 3000 metres for the second 2 inches, and an average of 6850 metres for the next 11 inches. (These results would be more valuable if we had a description of the blasting gelatin, the percentage of nitro-cotton and its content of nitrogen—also the physical characteristics of the explosive—its hardness, plasticity, etc.).

Velocity of Detonation Through Air.—The d'Autriche method was also used to determine the velocity of transmission of detonation through air. The cartridges ($1\frac{1}{4}$ in. x 8 in.) were put in a strong paper tube with an air spacing. It was found that the 60 per cent. "straight" dynamite had a range of 48 inches, and the 40 per cent. a range of 40 inches, and so on down to 20 per cent., with a range of 32 inches. The velocity was measured for every 5 inches of the intervening space. It was proved that the velocity of the detonating wave decreased rapidly with the distance. For the first five inches it was generally a little below the normal for the explosive itself, but fell off rapidly with the increasing distance. The average for the 40 per cent. was 2253 metres per second for the range of 40 inches.

The author's theory is that the normal velocity of the detonating wave through air is that of sound, or 340 metres per second, but this velocity conforming to the properties of the waves of sound and other waves of compression and rarefaction, is greatly increased at the high temperature and pressure,

which exist in the immediate vicinity of the detonation—rapidly decreasing, however, as the temperature and pressure decrease with increasing distance from the explosive.

(This is equivalent to saying that the detonating waves are transmitted through air according to the laws of sound, and degenerate into sound waves as the temperature and pressure fall with increasing distance. But when the velocity falls below a certain limit depending upon the strength and sensitiveness of the explosive, the waves are no longer capable of causing detonation.)

One interesting observation is, that the velocity of detonation in the second cartridge, if detonation is produced at all, is normal and independent of the degeneration of the wave in air. The most remarkable case of the detonating wave in one medium exciting a velocity greater than its own in another, is the action of the 40 per cent. "straight" dynamite on the high grade "gelatins."

General Comments on the Paper.—The introduction of the d'Autriche detonating fuse is of record importance in the study of explosives, and ought to lead to a new development of economy and efficiency in practical blasting. It gives the mine manager a ready means of determining the velocity of detonation of an explosive, and the relation this bears to efficiency in rock-getting. The so-called high explosives vary greatly in their normal velocities of detonation, which are found ranging from 26,000ft. down to 6000ft. a second. Every chemical composition may be considered as having a normal rate of detonation, but even this velocity must be defined as pertaining to a definite degree of confinement, and the use of a detonator of adequate strength. The rate of detonation of some explosives is much more influenced than others by the degree of confinement and the strength of the detonator. In some the physical condition of the explosive has great influence (this is not touched upon in Dr. Comey's paper), and some can have their velocities greatly increased by the use of a primer of different composition.

It is generally assumed that the higher the velocity of detonation of an explosive, the greater its efficiency in rock-get-

ting. There is this justification for the belief—a maximum rate of detonation implies a perfect detonation, whereas an abnormally low rate may denote insensitiveness and probably an incomplete metamorphosis. It does not follow—provided the condition of perfect detonation be fulfilled—that the maximum rate is the most favourable for rock-getting. For certain special purposes, such as “plastering” or surface blasting of boulders, the highest possible rate under the circumstances is undoubtedly desirable, for in this case the confinement is slight, and the rate of application of the energy must be of lightning quickness to effect the purpose. In blast holes, where the explosive is well confined, and expends its energy to greater advantage, it is probable that a medium velocity of detonation will be found generally to do more useful work for a given energy in the explosive. When the energy of an explosive is applied at the maximum rate, it is reasonable to suppose that the local effect in pulverising and heating the rock in immediate contact with the charge will consume an undue proportion of the energy—a portion which would have been expended in the more useful work of disrupting and removing rock masses if the application had been more gradual.

Blasting gelatin varies considerably in velocity of detonation, depending upon its composition and physical condition. It is believed that a blasting gelatin of normal rate is more efficient in rock-getting than one which, by composition, instability, or other cause, is of maximum quickness.

Gelignite seems to have normally a low rate of detonation. It is believed that if this can be somewhat quickened by use of a primer, its efficiency as a rock-getting explosive will be generally improved. In the special case of insensitiveness there is no doubt that the use of a suitable primer is called for both to correct this trouble and to develop the full energy of the explosive.

[These comments are general and off-hand. In future chapters I propose to treat the “Detonation of Explosives” in more detail, and to show the bearing of our latest knowledge, or lack of knowledge of the subject, upon practical blasting.]

CHAPTER III.

Industrial Explosives.

Nobel's Dynamite.—Modern Dynamites.—Gelatinous Explosions.—Freezing.—Sensitiveness.—The "Hake Effect."

Nobel's Dynamite.—This, which normally contains 75 per cent. nitro-glycerin and 25 per cent. Kieselguhr or infusorial earth, is a paste, dryish and stiff, or soft and greasy, depending upon the absorbent power of the Kieselguhr. It has a slight compressibility which makes it quite safe against ordinary shocks, while it is readily detonated under confinement with a cap of moderate strength, such as a No. 5, though a No. 6 is believed to be better.

Modern Dynamites.—Kieselguhr dynamite has been generally replaced by more economical mixtures—Dynamites, with active bases or nitro-glycerin mixed with a dope, consisting of an oxidising agent, and a carbonaceous element which serves to absorb the nitro-glycerin. The principle involved in these explosives is to make all the ingredients contribute to the working energy, the nitro-glycerin playing the role of detonating agent to the dope mixture. This principle was clearly recognised by Nobel in his patent for No. 2 dynamite, and is now universally accepted, being embodied also in modern gelignites and gelatin-dynamites, but for a time it was decried by some authorities. Nobel's trade successors, possibly to uphold the supremacy of Kieselguhr dynamite, which was threatened by cheaper rival compositions, generally joined in the cry against it. Even Mowbray, enamoured of his liquid tri-nitro-glycerin, ridiculed it. He compared the linking of gun-powder elements with nitro-glycerin, to harnessing a locomotive to the electric current; one being relatively slow and the other quick, they could not pull together. Time and practical experience have completely refuted this a priori reasoning.

The principle received the fullest recognition in America, where three-fourths of the explosives made are still compounded upon this principle. The dope first used approximated closely the composition of gunpowder, but experience proved that better results could be obtained by discarding the sulphur and replacing the charcoal with a cellulose ingredient, such as wood pulp.

These American or "straight dynamites" (as Dr. Comey calls them in his paper; or "Lig-Dyns," as they are called at the Cape Explosives Works, in South Africa) are the most certain and regular of all forms of explosives in their response to the detonator; while they are also (when made with reasonable care) probably the safest explosives in use. The cushioning action of the cellulose absorbent in warding off the effect of friction or blows is extraordinary. This is due to the resilience of the absorbent. No matter how densely the cartridge is packed at the factory, there is a large margin of safe compressibility left to meet the exigencies of handling and use. I have made scores of tamping experiments by placing the cartridges in an iron pipe, putting in a hardwood tamping rod and dropping a heavy weight (about 35 pounds) upon the head of the rod from varying and increasing heights up to 16ft. By prolonging this rough treatment, I have always succeeded in driving the rod entirely through the column of cartridges, wedging the stuff against the sides of the pipe, and subjecting it to great friction and sharp percussion at each blow—without one instance of accident. I have made a few experiments of the same kind upon Kieselguhr dynamite, and upon a nitro-cellulose gelatin, which was nearly the equivalent of modern gelignite. I got one small, sharp explosion with the first, and the second, in one test, took fire and burnt without explosion before the experiment was completed. If the lower end of the pipe had been closed, as in a bore-hole, it is possible that an explosion of low order would have resulted. While the Lig-Dyns show themselves immune to ordinary friction and percussion, they are specially susceptible to the vibrations produced by the detonator, and detonation once properly started is transmitted with great certainty and regularity. Dr. Comey shows,

moreover, that if two 1 $\frac{1}{4}$ in. x 8in. cartridges are confined in a strong paper tube, one cartridge will explode the other, while they are separated by a considerable air gap. The 60 per cent. has a range of about 48in., and the 40 per cent. one of 40in. Though the detonating wave in air is subject to a rapid deterioration in velocity, the second cartridge, if exploded at all, detonates at the normal rate. This peculiar susceptibility of the Lig-Dyns to detonation, I ascribe to their physical structure. This is more or less open and loose, and the minute, but intense vibrations of the detonating wave can always penetrate the surface, and find a multitude of points for molecular attack. Ordinary shock attacks the stuff in mass, and is absorbed without causing explosion.

Gelatinous Explosives.—The gelatins, including blasting gelatin, gelignites and gelatin-dynamites, contain nitro-cotton, which unites more or less perfectly with the nitro-glycerin, and converts it into a jelly. Blasting gelatin contains, or should contain, nothing but nitro-cotton and nitro-glycerin, usually about 8 per cent. of the former to 92 per cent. of the latter. There is no distinction between gelignites and gelatin-dynamites, except that of grade. Some manufacturers use the second name for a higher grade, others for a grade lower than the gelignites, which generally carry from 60 to 70 per cent. of nitro-glycerin. These gelatins contain a dope similar to that of American dynamite—usually wood pulp with a nitrate. They therefore need less nitro-cotton in proportion to the nitro-glycerin than blasting gelatin. The great advantage of these compositions is that the nitro-glycerin, being reduced to a jelly, requires less absorbent to hold it, and enough nitrate can be introduced to give very complete oxidation of the products. This can be done in the middle and lower grades of Lig-Dyns or American dynamites, but is impossible in the higher grades unless some inert absorbent is used to help the wood pulp.

Blasting gelatin is the ideal explosive when a maximum of power is required. It was Nobel's crowning triumph in industrial explosives. Not only are its physical properties specially suited to its work, but as an embodiment of energy it is re-

markable for uniting two explosives—nitro-glycerin and nitro-cotton, so that the defect of one is made to compensate for the defect of the other. Nitro-glycerin, when fully detonated, is wasteful of energy in giving an excess of oxygen—about 3.5 per cent. of its weight—while nitro-cotton is deficient in oxygen, and produces a large percentage of carbon monoxide. When the proportions in blasting gelatin are normal, and the grade of nitro-cotton good, this excess and deficiency compensate each other very accurately, and there is no waste of energy. General Abbot found in his submarine experiments that blasting gelatin gave the greatest intensity of all the explosives tried. The gelignites partake in composition of the nature of blasting gelatin and of the Lig-Dyns. They are more plastic and denser than the latter, and have the advantage of being more easily oxidised, as before stated.

Neither blasting gelatin nor gelignite is very susceptible to detonation. Both require strong caps to start a proper detonation, and the wave is easily interrupted by air gaps or other obstructions. The wave is also subject under favouring circumstances to a deterioration in its own medium, as will be shown in a later chapter. Blasting gelatin under proper conditions gives a wave of high velocity, but it does not appear to have the detonating power of the Lig-Dyn wave, though this in its own medium is much slower. Gelignite has normally a slow rate, but this can be greatly increased by firing it with a Lig-Dyn primer. It can be laid down as a practical rule that all high explosives require strong confinement for complete detonation. (It has been seen that even so sensitive an explosive as mercury fulminate requires this first element of detonation.) Even if this condition, which applies with special force to gelatinous explosives, be fulfilled, a detonator of adequate strength must be used to develop the full power.

The Lig-Dyns, when confined, can be detonated with apparently full force by a No. 5 (12.3 grains) cap, but even in this case it is believed a No. 6, containing 1 grammé of fulminate composition, is better and surer. In connection with the subject of detonation there must be noticed a property peculiar to nitro-glycerin and its compounds.

Freezing.—Nitro-glycerin freezes, and becomes solid at moderately low temperatures—about 45-46deg. Fahr.—and all explosives containing it are subject to the same drawback, but in different degrees. When the liquid is solidly frozen it is virtually inexplosive—the strongest detonator seems to have no effect upon it. Mowbray utilised this property in making it safe for transportation. He prepared special tin cans for holding it, with a centre cylinder to contain ice. He proved that in the frozen condition it would stand very rough treatment. Notwithstanding this, many accidents have happened with frozen dynamite and other explosives, and miners have a wholesome dread of handling them in this state.

An experiment which I made many years ago throws some light on the subject. I took a solid lump of frozen nitro-glycerin, rather larger than a man's fist, scraped a groove in the top of it, brushed out the dust, and fired a strong detonator in the groove. The detonator broke the lump into perhaps half-a-dozen large pieces, but there was no explosion. Without removing the dust and small bits, I gathered all the fragments and fired a detonator in the pile. This time there was a sharp explosion, and many fragments were made and scattered over the brick pavement, which served as a floor for the experiment. The fragments were carefully gathered up once more and fired. The result was apparently a full detonation. The brick upon which the pile was fired was smashed, and a small depression made in the pavement. The weather was very cold, and at no time during the experiment was even a trace of liquefied nitro-glycerin noticed.

The natural conclusion is that frozen nitro-glycerin is readily detonated if broken into small pieces. The danger in handling frozen dynamite probably comes from fine crystals of nitro-glycerin forming either inside or outside of the cartridge wrapper. These are reported to be specially susceptible to friction, like the fresh crystals of potassium chlorate, but the subject is very obscure, and little is known about it.

Kieselguhr dynamite, when solidly frozen (as in the packed cartridges) is practically inexplosive, yet General Abbot adopted it as his standard explosive for submarine mines. In

cold waters it naturally freezes in winter, and it puzzled some dynamite men to account for such an error of judgment on the part of this distinguished officer. General Abbot, however, discovered that by a simple expedient he could keep the dynamite sensitive to detonation. He loaded his torpedo cases loosely with granulated dynamite. Freezing in this condition made little or no difference to detonation with a strong exploder.

In America a specialty is made of low-grade dynamites for railway work, bank blasting, etc., as cheap substitutes for black powder. A favourite grade is 5 per cent. The mass usually consists of a granulated mixture of nitrate and bituminous coal or the equivalent, to which 5 per cent. of nitro-glycerin is added. When finished the stuff is packed loose in the wooden cases. A Lig-Dyn primer is generally used to fire it. I have often noticed that this explosive detonates readily in the coldest weather.

In commenting upon the susceptibility of Lig-Dyn, I ascribed this to its texture, which is comparatively loose and open. Lig-Dyn when frozen will still explode, though not perhaps with full force. In fact, the freezing of nitro-glycerin always handicaps to some slight extent its own detonation, or the detonation of its mixtures or compounds. This is on account of the latent heat of fusion, which absorbs some of the heat of the detonating wave, but whether these explosives will detonate at all generally depends upon their state of aggregation. In solid mass they offer an extraordinary resistance to detonation, but if granulated or finely divided, detonation is comparatively easy. The explanation is that the intense vibrations of the detonator have a thousand points of attack at which an extensive molecular disturbance can be set up. A frozen cartridge of Kieselguhr dynamite is a type of the resistant condition. Certain substances have a slow, hardening action upon nitro-glycerin. Various resinous matters, like ordinary colophony (common resin), when present as ingredients in dynamites have this effect. The first No. 2 dynamites made in America generally contained a large percentage of resin. In the course of time the cartridges became as hard as wooden sticks, and nearly as inexplosive.

Sensitiveness.—This is a complicated subject into which many factors, both chemical and physical, enter. Every explosive may be considered to offer a specific resistance to detonation. The most important element in this is its chemical constitution, but to go into this would lead us into too broad a discussion. The heat of formation of a compound is, in a general sense, a measure of its stability—that is, a measure of the energy taken as heat which must be applied to it to bring about decomposition. I may here remark that detonation by heat itself so applied that all parts of the explosive body are brought to the critical temperature at the same time, is probably one of the most perfect forms of explosion. The atoms in their increasing swing reach the limit of stability nearly simultaneously, and the resistance to detonation is almost nil at the moment of the “let go.”

Some explosives by chemical nature are so unstable as to be of no practical use. Such are nitrogen chloride and iodide, which even give out heat in breaking up into their elements. These are called endotherms, which is equivalent to saying that they have minus heats of formation. But instability arising from chemical constitution does not concern us just now in a discussion of industrial high explosives. Our first point seems to be that these, when in hard, solid masses, offer great resistance to detonation, but if the masses are broken up, and finely divided, they can be readily detonated. This was illustrated in the case of frozen nitro-glycerin and frozen dynamite. The susceptibility of Lig-Dyns to the detonator is also related to the state of aggregation. These have a loose, somewhat open, texture, and the vibrations of the detonating wave can penetrate the surface and make an effective attack. Coming now to gelatinous explosives, which from their nature resist this form of attack, it is found that the sensitiveness depends upon a different property—viz., the consistency. If this is either hard or elastic they will be difficult to detonate. India-rubber, or caoutchouc, is of known substances one of the most resistant to the disintegrating action of an explosion. Cloth faced with rubber, as noted in a previous chapter, will preserve its structure when subjected to the cyclonic action of an explosion, in

which stout timber will be completely destroyed. It is possible to make a gelatin of a consistency closely resembling caoutchouc by gelatinising the nitro-glycerin with an excess of nitro-cotton. Such a gelatin will need a very powerful cap for detonation. A still further excess of nitro-cotton will give products like hard rubber or gutta-percha—analogous to cordite or ballistite, both of which are incapable of detonation in mass.

Blasting gelatin and gelignites are by nature more insensitive to the detonator than Lig-Dyns. It may be laid down as a principle that they require stronger confinement and heavier caps for full detonation. Their sensitiveness, however, can be varied much in manufacture, as it depends chiefly upon the consistency. Soft, plastic gelatins are more easily exploded than hard elastic ones.

The "Hake Effect."—These explosives, even when made of normal consistency, are subject under conditions that are somewhat obscure to a change during storage, by which they become very insensitive. I have called this the "Hake effect," in honour of Mr. C. Napier Hake, the late Inspector of Explosives for the State of Victoria—a gentleman to whom the manufacturers of gun-cotton owe several very valuable investigations. Though this effect is well known to dynamite makers, I believe Mr. Hake to be the first man of science outside of their ranks to make a study of it. He has made this curious and interesting observation. If a small percentage of blasting gelatin that has become insensitive through this effect be re-worked and mixed with a large percentage of a fresh lot, it will infect the mass, and the re-made blasting gelatin will soon undergo the change. Something more than a mechanical effect is therefore concerned; in fact, an obscure form of catalytic action seems to be indicated.

The usual view taken by the manufacturer is something like this: When a gelatin is made, a certain proportion of the nitro-glycerin enters into a firm union with the nitro-cotton, while part of it remains free, occluded as it were in the pores of the jelly. It is mainly this free portion which gives plasticity and sensitiveness to the gelatin. If now by a slow gelatinising action the free nitro-glycerin is taken up by the

nitro-cotton, the gelatin stiffens, becomes harder and more elastic, and is likely to develop the "Hake effect" in storage.

Much depends upon the gelatinising power of the nitro-cotton. This varies greatly, and no absolute rule has been formulated for making it of the highest quality. Great care in the selection of the materials, and accuracy in maintaining the proportions of these, as well as the conditions of time and temperature during the process of manufacture, are the elements of success. The percentage of nitrogen in the nitro-cotton is not a criterion of its gelatinising power, except in a general way. Now, 7 per cent. of one nitro-cotton may give a gelatin of normal consistency, to obtain which would require 9 or 10 per cent. of another nitro-cotton of inferior gelatinising power. Nevertheless, it is held by some persons that it is always risky to use so much, because they believe that time may bring about a complete gelatinising effect even with the inferior quality. According to this view, a high quality differs mainly from the inferior quality in being quicker in its action. There are so many unknown factors concerned in the "Hake effect" that it is impossible to take them all into account. One of these is the condition of storage, especially the temperature. The manufacturer must make his stuff rapidly. At most, he can only give an hour or two to gelatinisation. His general aim is to make the highest quality of nitro-cotton possible, to use as little of this as will give the right consistency, and to exhaust its gelatinising powers by stimulating these with heat. He therefore gelatinises at a high temperature. The decision, whether the gelatine, when finished, is of the right consistency to meet the exigencies of storage and use, should be made under uniform conditions of temperature, summer and winter. If this point is neglected, summer-made gelatin is liable, in the exigencies of service, to prove insensitive—and that made in winter is apt to develop exudation. This is the practical observation of Mr. W. A. Hargreaves, Chief Inspector for South Australia. In my limited experience, the "Hake effect" is more likely to supervene if in storage a moderate temperature prevails—rather chilly than warm—though this may mean simply that heat tends to keep the gelatin

sensitive. If, however, a gelatin of normal consistency and sensitiveness, which has been stored in a comparatively high temperature, is subjected for a few months to a low temperature, it seems to develop the "Hake effect" very promptly. On the other hand, a gelatin which threatens to develop the "Hake effect" may show normal sensitiveness at least for a time if transferred to a warmer climate.

CHAPTER IV.

Australian Conditions.

Exudation of Gelatins.—Tests for Sensitiveness.—Open Tests.

Exudation of Gelatins.—The matters treated in the last chapter assume great importance in Australia, where, in every State, there is a strict system of inspection, and where storage may be unusually prolonged. The manufacturer is, in fact, between two fires. The inspectors favour firm, elastic gelatins, in which the nitro-glycerin has been very completely taken up by the nitro-cotton. The miners, on the other hand, prefer gelatins which are soft and sensitive.

A gelatin of plastic consistency, when freshly made, will generally show in a little while after storage a narrow line of free nitro-glycerin along the edge of the inner fold of the wrapper. There seems to be a strong capillary attraction along this line, probably due to the double fold, which tends to draw out of the jelly the free nitro-glycerin near it. If this line shows more than a trace of free nitro-glycerin, the inspector will condemn the stuff as exuding, and order it to be rewrapped. If the nitro-glycerin extends into the folds, it may be destroyed. If, on the other hand, this line is absolutely absent, then under the conditions prevailing in the mines at the present time, the stuff is likely to be condemned by the practical users as being insensitive. If such a stuff is stored for many months before use, it is likely to develop the "Hake effect," and become very insensitive to even a proper detonator.

The trouble arising from the inspector and the practical miner being so far apart in their ideas as to the right thing, has been aggravated in Australia by what I consider a false standard of sensitiveness. Unfortunately, it has become the

fashion to use the minimum detonator for exploding gelatinous explosives. The miners' standard is the No. 6 cap. If the stuff does not work with this, he condemns it as no good. There is only one sure certificate that a gelatin will detonate with so light a cap as this. It must have enough free nitro-glycerin in it to develop, under ordinary conditions of storage, the line along the inner fold referred to above; but this is what the inspector objects to. In so practical a country as Australia, it seems strange that such a lack of co-ordination should exist. But the inspectors are conscientious, over-worked officials, who cannot find time to visit the mines and confer with the mining men. If they could do this, doubtless steps could be taken to bring the two standards into accord. The matter is a serious one. Several thousand cases of explosives made by conscientious manufacturers are "re-conditioned," and some hundreds destroyed every year. If the miners' standard must be accepted by the manufacturer, the inspector ought not to apply tests which were appropriate twenty years ago, but are now out of date. The tests laid down in the Regulations were adopted when blasting gelatin was a different thing from what it is now. The gelatin of Alfred Nobel and his immediate successors is not in vogue in Australia. The standard has been perverted. It is no longer a slightly elastic, translucent mass, without a trace of free nitro-glycerin on the surface, but usually a soft, mushy substance, with the line of nitro-glycerin well developed, even if it is not exuding or on the border line of exudation. If one examines the circulars issued by Nobel himself, or by his authority, giving the properties of blasting gelatin, he will find it stated that this explosive is not suited to breaking boulders by surface action or for chambering—"bulling" holes where the confinement is not good, and there are still old-fashioned blasters who will not use it in this way. I found one such noble old patriarch at Mount Morgan, who insisted upon having Kieselguhr dynamite for "bulling" his holes, and got it, too. I was much surprised when I came to Australia to find that both blasting gelatin and gelignite were used for "plastering" or breaking boulders by surface blasting, and apparently with good effect. In fact, it has become the fashion

to make the stuff sensitive enough to explode with great power under the slight confinement of a few handfuls of damp clay plastered over it. "C'est magnifique mais ce n'est pas la guerre." The stuff that is capable of doing this is not blasting gelatin, as Nobel, and even more modern "old fogies," like myself, have understood and admired it. The point is that this degree of sensitiveness cannot be conferred upon it without sacrificing some of its greatest qualities, as I hope to show later. To an "old fogy" it savours of Charlatanism to pervert a noble (Nobel) explosive from its real purpose, in order to fit it for such an meretricious service as smashing boulders by "plastering"—especially in these days of hand-pneumatic drills for making "pop" holes.

The reform should begin at the bottom. A proper strength of detonator should be adopted as the standard for gelatinous explosives. In other words, the detonator should be made for the explosive, and not the explosive to suit the detonator. This should certainly not be less than No. 7; or, better, No. 8. In South Africa, where a more progressive policy has been followed, No. 8 is nearly the universal standard. This gives the manufacturer a reasonable working margin. His product need not be so sensitive, that it has to run the risk of rejection or "re-conditioning" by the inspector, while the latter can maintain his high standard without either penalising the manufacturer on the one hand, or, on the other, compelling the miner, with his weak detonator equipment, to accept stuff bordering upon insensitivity.

Tests for Sensitiveness.—Like the "proof of the pudding," the best test of an explosive is to fire it under the conditions of use, but this test is not always practicable, especially at the factories. The factory is fortunate that has even a quarry of hard rock near at hand, in which trials can be made.

Speaking generally, the rifle bullet is a detonating agent for industrial explosives. A few, such as Tonite, now out of date, an explosive made of ground guncotton and barium nitrate, compressed into hard cartridges, would resist it, but these have not found favour in mining.

One of the earliest tests that I adopted was to hang up a cartridge ($1\frac{1}{4}$ in. x 4 in.) by a string, and blow it to pieces, at, say, 10 paces, with a shot gun. As an aside, I may say that it is easier to hit so small an object with a shot gun than with a rifle, but I found it, moreover, a good rough test of sensitiveness. If the cartridge seemed to explode fully, I concluded from previous experiments that it could be trusted to detonate perfectly in the bore-hole with a No. 5 cap (about 12 grains of fulminate composition). At that time I made only one explosive (patented under the name of Detonite), which would resist this test. This contained a nitro-cellulose made from wood fibre mixed with 68 or 70 per cent. of nitro-glycerin and a nitrate—nearly the equivalent of modern gelignite. It was a dense, rather hard, dryish mass, absolutely free from exudation, with about the plasticity of moist plug tobacco. It required a very strong detonator, which I was fortunate enough to get from the local factory. This explosive was more than a match in energy for the strongest dynamites of the day, and showed good all-round qualities in use. The gelatinisation was in the cold, and gave time for the cartridge to be packed like ordinary American dynamite. The nitro-cellulose was a good absorbent as well as gelatinising agent for the nitro-glycerin. Not a trace of free nitro-glycerin was ever observed in the packed cartridge.

Blasting gelatin can be made immune to the rifle bullet, but only at the expense of its general serviceability. It is said that a small percentage of camphor added to the composition will have this effect.

Open Tests.—The so-called “open tests” for sensitiveness, made with detonators, are instructive, but the results are apt to lead to wrong conclusions if the general principles of detonation are not kept in mind. In 1904 I made some experiments on the Ferreira Deep slimes dump, at Johannesburg, which illustrate some of the properties of the gelatins in regard to detonation. The explosive was a rather sensitive blasting gelatin; in fact, some of the cartridges showed signs of exudation. The site was a level stretch of compact damp sand. A piece of timber 3 in. x 9 in., 24 ft. long, was laid down, and the

cartridges— $\frac{7}{8}$ in. by 4in.—forming a long string, were placed on it and pressed together end to end, but without removing the wrappers. About 18in. of damp sand, taken from a bank near by, was shovelled over the string as it was formed. An attempt was made to detonate the string from one end. Out of about a dozen trials, in only one case did we succeed in exploding the whole string—some 20ft. in length, and this was with a No. 6 cap. The timber and the compact sand gave very good records of the energy of the detonation in its progress along the string. The excavation, which was sharply and clearly defined, reached a maximum about 4 or 5ft. from the detonator end. Here it was about 5ft. wide, and about 3ft. deep. From this point it tapered pretty regularly in both width and depth to nearly nothing at the further end. The timber gave equally clear indications. For the first 5 or 6ft. it was reduced to match-wood and splinters. The splinters became larger along the line, then the timber was broken into short lengths, then into longer lengths, and at the further end a piece some 4ft. long was barely split. In all the other trials made, some with No. 6 and some with No. 8 detonators, the detonation broke off short from 2ft. to 2ft. 6in. from the detonator.

The conclusion is that under conditions of poor confinement, the detonating wave in gelatins is subject either to a sharp break or to a dying out. The exact point of the break off was probably determined by an obstruction, such as an extra thickness of paper in the end cartridge fold; but it is very remarkable that this point should have varied so little in the different experiments, as if the detonating impulse of the cap had something like a definite range. The dying out or deterioration in the detonating wave is still more interesting in showing an enormous possible variation in the rate of detonation of gelatins. This phenomenon is rare, and I was fortunate in obtaining the effect in the open.

Both effects, the break-off and the dying out, undoubtedly obtain in rare cases, even in the bore-holes, where unexploded cartridges are sometimes found, especially when a charge has not broken to the bottom, but has left a "socket." This may be the result of either insensitiveness in the explosive, or to the

use of a defective or inadequate detonator. This should be carefully distinguished from another form of accident in which unexploded cartridges may also be found. An explosive is sometimes credited with a "socket" and unexploded cartridges, when it is not in fault, and the foreman or shift boss should report a "cut hole"—that is, a hole which has not been fired normally by the detonator, but by an adjoining blast, the rocks from which have cut the fuse. In prosecuting open tests, I have exploded many cartridges on a sandy beach, noting the air gaps necessary to prevent the detonation of one cartridge by another. The most striking observations are the small excavation made even by the primary cartridge, and the minute air gap sufficient to break the communication of the detonation.

Another form of open test is sometimes practised. A certain number of cartridges, say, six $1\frac{1}{4}$ in. x 4 in., stripped of their wrappers, are welded together, end to end, on the ground, and then the string is fired from one end. If 4 or 5 out of the 6 explode, no matter how, the stuff is pronounced good. If only 2 or 3 out of the 6 explode, it is pronounced insensitive. This test has its value in the hands of the expert, though it is remarkable for ignoring the conditions of the bore-hole, where the wrappers are not removed, the cartridges are not welded (it would be a good thing if they were), and the confinement, instead of being nil, is perfect. The objection to the test is that absolutely wrong conclusions may be drawn from it. For under this unnatural condition of no confinement a No. 6 detonator shows as much power as a No. 7 or No. 8. In fact, in my experience, for all tests made without proper confinement, the No. 6 gives generally the best results, and it is not hard to conceive a reason for it. The column of explosive not being confined, the portion surrounding the cap is likely to be blown away by the action of the strong detonator, without contributing to the creation of a normal wave in the column. Many experimenters have noticed an effect of this kind when detonating explosives under slight confinement, and some have concluded that a detonator may be too strong. This conclusion is warranted when it is limited to the conditions of the experiment, but in the bore-hole, where the dissipating effect just

noticed cannot take place, the detonator cannot well be too strong. I believe that the employment of the "open test" for sensitiveness has had much to do in Australia with fixing the grade of detonator for gelatinous explosives so low as the No. 6, and, again, this has reacted upon the standard of gelatins as to consistency.

To be fair to the older explosives companies, who have had much to do with fixing these standards, it is well to take into account the conditions of the country with its great range of latitude and variations of climate, as well as the long storage to which explosives are often subject. It may be that the "Hake effect" caused such large losses in storage under the old standard of consistency that they found it a choice of evils to make a soft sensitive gelatin less subject to this effect, although in doing so they ran counter to the standards set by the Inspectors, and have had to suffer from occasional "reconditioning," or even total loss by exudation.

CHAPTER V.

Theory of Explosive Energy.

Energy of Explosives.—Uncertainties of Science.—Theory of Explosive Energy.—The Chemical Equation of Metamorphosis.—Dissociation and Lack of Reliable Scale for High Temperatures.

Energy of Explosives.—As this is a subject which I have been studying both practically and theoretically for thirty years, I can talk about it pretty glibly. But it is too big a subject to be handled in a few columns of print. If one attempts it, he finds himself in trouble. Besides the difficulty of condensing a treatise into so small a compass, the writer is forced to state propositions which no one disputes, in the same off-hand way that he states those which his study has led him to adopt, but which may not be acceptable as orthodox to some of his readers. He may have strong arguments and abundance of facts to support his views, but he cannot bring these forward without being tiresome. He must appear to dogmatise when he would prefer to demonstrate.

Uncertainties of Science.—Energy is the only thing we know to exist. Our impressions regarding everything else are derived from the action of energy in its varied forms upon our senses. Therefore, energy is the only reality. All other things may be such stuff as dreams are made of. Matter may be holes in the ether, or local condensations, or vortices in the ether or portions of the ether carrying more or less, or a different kind of energy from the usual, but in the last analysis we know nothing about its constitution. As to the ether itself, its properties surpass our comprehension. We know it has a reality, as the vehicle and store house of the energy of the universe, but we cannot form a conception that will cover it.

A thing that is more than a million times lighter than rarefied hydrogen, and yet has an elasticity comparable with tempered steel, is too difficult for our minds to grasp. However, I propose to avail myself of some old-fashioned ideas, which are fortunately not yet extinct. The conception of matter as substance, distinct from energy, is one that has grown up with and taken firm root in the human mind. We have accumulated a mass of impressions in regard to the two, which we consider knowledge, and we have classified and arranged some of this and called it Science. Twenty, thirty, or even forty years ago, our Science was more cocksure than it is to-day. We had something we could tie to. The Conservation of Energy, the Permanence of the Atom, the Indestructibility of Matter—these were the sheet anchors—some of which seem to be dragging to-day.

Theory of Explosive Energy.—For inspiration we accordingly hark back to the good old days when we held settled notions. The view which I have adopted in my study of explosive energy runs something like this: Matter has a grained structure, is built up, in fact, of atoms and molecules. The gaseous form of matter is that in which its properties are the least complicated. The action of heat or energy upon this form of matter is governed by simple laws. A gas which obeys these laws with accuracy is called a perfect gas. The conversion of solids into liquids, liquids into vapours, and vapours into permanent gases, by elevation of temperature, shows a progressive approach towards this state of perfection which we believe to be attained by all gases at temperatures sufficiently removed from their critical points. We therefore hold that the laws of gases are applicable to the products of an explosion—provided the first condition of these laws—equilibrium or uniform distribution of the energy, obtains in the products.

The law of Avogadro-Gerhardt that equal volumes of all gases contain at the same temperature and pressure equal numbers of molecules, as well as the hypothesis which we owe to Clausius, that the specific heats of gases in the perfect gaseous state are constant, and the same for those containing equal numbers of atoms in the molecule, is each, according to our

view, a rigid deduction from the ideal behaviour of gases in the perfect gaseous condition.

Explosive energy can be studied under two different aspects, depending upon whether the energy is developed without the performance of mechanical work, or whether the development is accompanied or followed by the performance of mechanical work. We have two corresponding ideal conditions:—

- (1) Confinement of the products at constant volume.
- (2) Adiabatic expansion of the products.

Both involve the ideal conception of an "initial state" in which the energy is fully developed. The first is fulfilled by supposing the explosive to be fired in a closed vacuous vessel impervious to heat, strong enough to retain the products. The second, by supposing the products to develop their energy fully, and then to expand so as to perform mechanical work without communication of their heat as such to surrounding bodies.

In the first case, if the vessel be impervious to heat, the energy will be conserved indefinitely. In practice, the greater part of the energy will be dissipated in the form of heat communicated by radiation and conduction to surrounding bodies. A portion of the energy, however, will be retained. It is that which pertains to the gaseous products in their ordinary or standard state. The portion lost, which can be directly measured, is the heat of decomposition, or heat of the reaction.

In case (2), if we suppose the expansion to be continued indefinitely the whole of the energy will be transformed into work. The condition of indefinite expansion is irrealisable. The limit of the expansion is fixed by the presence of a subtle medium—the atmosphere which surrounds all terrestrial objects. The pressure of the expanding products cannot fall below the pressure of the medium. This gives a natural limit to the work that can be realised.

Returning to case (1), confinement of the products to a closed vessel, we find that the most marked manifestation of the energy is the pressure on the interior walls of the vessel.

This is sometimes erroneously confounded with the energy itself. Only a portion of the energy of the products is concerned in the pressure. This we may call the Kinetic energy. There is another portion which is dormant so far as the dynamic effort of the gases is concerned. This we may call the Internal energy. The pressure is the intensity factor of the Kinetic energy, the capacity factor being volume. One cannot be increased except at the expense of the other—that is, the pressure will be higher as the confining volume is less. The Kinetic energy, however, remains constant.

When the products expand adiabatically, it is the Kinetic energy which performs mechanical work, but gases have this wonderful property—as the Kinetic energy is expended in work it is replenished by drawing upon the stock of Internal energy, so that the two diminish together, and if the expansion could be continued indefinitely, the whole energy could be transferred into mechanical work.

If we consider the work as limited by some condition, such as the attainment of a certain degree of expansion by the products, then the work done will depend upon a general principle of energy—viz., that its availability increases with its intensity factor. That is, the higher the initial pressure or tension, the greater will be the proportion of the energy that can be transformed into work.

The potential of an explosive is its total energy, or the dynamical equivalent of the heat of decomposition, plus the energy which the products possess in the standard state. The necessity for this addition arises from the fact that the heat is measured from the standard state of the products, and does not include their energy in this state. The standard state may be taken as 0° C., and one atmosphere; or, to be exact, a barometric pressure of 760mm. of mercury, or about 2116.3 pounds on the square foot.

The Available Energy or Maximum Work is that portion of the potential which theoretically can be converted into mechanical work. This is limited by a general condition, the presence of an atmosphere with a definite pressure which surrounds all terrestrial operations. For a given initial state of

tension, the available energy is therefore that portion of the potential which can be converted into work by an adiabatic expansion from the given state of tension down to an equilibrium with the atmosphere. The available energy will be found greater as the initial state is taken nearer the state of absolute density of loading, or that in which the products are confined to the volume occupied by the explosive itself. The Useful energy or Useful work is that portion of the available energy of the products which can be applied to any special object. It is equal to the available energy less the dynamical equivalent of the heat lost as such by communication to other bodies, and the energy expended in useless work.

The Chemical Equation.—If we can write the chemical equation of metamorphosis of the explosive, and have at command certain physical data, we can make an interesting study of its energy. If we write the gaseous products in molecules, double the exponents, and place the figures above the corresponding symbols, and also write the molecular masses below the symbols in both members of the equation, it will facilitate our study. We can take these masses in any units we please, grammes, pounds, etc. If we take them in Criths, the figures above the symbols will represent units of volume in the standard state—a crith being the mass of hydrogen corresponding to the unit volume. The French crith is .0896 grammes, the mass of a litre of hydrogen at 0° C. and 760mm. The British crith is .005592 pounds—the mass of one cubic foot under the same conditions. In this way, we can readily calculate that one pound of nitro-glycerin will give 11.423 cubic feet of gas when the products are cooled down to 0° C., and are under one atmosphere of pressure. The study being theoretical, we take water (H_2O), which is one of the products, as a gas in this state—that is, we apply Avogadro's law as though all the products were perfect gases. This volume, 11.423 cubic feet, corresponding to one pound, may be called V, the specific volume.

To calculate the heat of decomposition, we must have the heat of formation of the explosive itself if it is a chemical compound, or the heat of its several elements if it is a mixture.

We must also have the heats of formation of the products. By adding the heats of each member of the equation together, and deducting the sum for the first member from that of the second, we get the heat of decomposition, H. Dividing this by the molecular mass of the explosive, we get the heat h for one unit of mass. The thermochemists do not agree exactly in the experimental determinations of heats. According to the researches of McNab and Ristori, the heat of decomposition of one unit of nitro-glycerin (H_2O taken gaseous—as it should be in energy calculations) is 1535 heat units. Relying upon earlier experiments, I have usually taken it lower in my calculations, viz., about 1483 units. The heat unit is the specific heat of water. Theoretically, this is taken at its maximum density, so that there is no internal work done by expansion during the rise of temperature $1^\circ C$.

The potential or total energy for unit of mass is $E = J.T.kv. = J.t.kv. + J.273kv.$, in which J (called a Joule, in honour of Dr. Joule, of Manchester) is the dynamical equivalent of the heat unit. As we use centigrade degrees, when the unit of mass is one pound, this is about 1396 foot-pounds; T is the absolute initial temperature of the explosion, t is the rise in temperature from $0^\circ C$. and kv is the mean specific heat (at constant volume) of the products. The energy due to the heat is $J.t.kv.$ The energy of the products in the standard state is $J.273kv.$

$$T = t + 273\text{deg.} \quad t = \frac{h}{kv} \text{ or } \frac{H}{Kv},$$

in which h is the heat for one unit of mass (we take this as one pound) and H the heat of the reaction, kv is the mean specific heat, and Kv is the total specific heat of the products of the reaction.

Considering the case of confinement at constant volume, the Kinetic energy E_k of the products in such a state is equal to $\frac{3}{2} PV$, in which, for the purpose of simplifying calculation, P is taken as the pressure when the products are confined

to V the specific volume. P can be readily calculated from the formula

$$P = \left(\frac{h}{273kv} + 1 \right) 2116.3$$

in which P is taken as the pressure on the square foot for the unit of mass, one pound detonated in the specific volume of the products expressed in cubic feet. The term within the parenthesis is the pressure in atmospheres, the whole term is the pressure in pounds. As defined in foot-pounds the Kinetic energy is independent of any conditions except that unit mass (1 pound), shall be considered, and the volume to which the products are confined shall be expressed in cubic feet. The product PV is constant. If the gases are confined to a smaller or larger volume the pressure is correspondingly increased or decreased according to Boyle's law.

Considering equal volumes, the Kinetic energies of all gases are the same at equal temperatures. The total energy which is proportional to the specific heat or energy—that is, the increment corresponding to 1 degree of temperature, depends upon the number of atoms in the molecule. If we take the specific heat of a diatomic gas as the standard of measure, that is, unity, the specific heat of a triatomic gas such as CO₂ or H₂O will be 1½—that of a tetratomic gas such as NH₃ will be 2, and so on. A monatomic gas which is rare in explosion products has the same Kinetic energy as the others, but there being no interatomic energy the Kinetic is its total energy, and is proportional to its specific heat. Referred to the diatomic standard, taken as unity, this is 0.615. The specific heat of a gas, whether of mass or volume, is independent of the heat unit employed, the comparison being with the specific heat of an equal mass of water.

The specific heat kv of hydrogen is 2.422. This is the specific heat of unit mass, and also the specific heat of the volume corresponding to unit mass. Volumes equal to this of all other diatomic gases have the same specific heat—2.422. This gives us a ready means of calculating from the data furnished by the chemical equation, the total specific heat of the products or their mean

specific heat. We take the volumes (figures written over the symbols), and reduce them first to the diatomic standard, and multiply their sum by 2.422. In the case of nitro-glycerin the volumes are 14.5—reduced to the diatomic standard, they add up 20. This multiplied by 2.422 gives 48.44, the total specific heat Kv for 227 units—227 being the molecular mass

48.44
of nitro-glycerin. The mean specific heat kv is $\frac{48.44}{227} =$
0.2134 nearly.

The specific heat we have so far used is that at constant volume kv. This is the true specific heat, because no work is done. It is therefore the real increment of energy for 1 degree of temperature. There is another specific heat—that at constant pressure, kp. This is larger because part of the energy is expended in the work of expansion of the gas against the constant pressure during the rise of temperature of 1 degree. The difference between the two is the work of this expansion. Hence we have the fundamental equation—

$$(A) \quad kp - kv = \frac{PoVo}{J.273}$$

in which Po is the standard pressure on the unit of surface,
 $\frac{1}{273}$

Vo the specific volume of unit of mass, $\frac{1}{273}$ is the increment
of volume for 1 degree in temperature, and J the dynamical

equivalent of the heat unit. This is introduced to reduce the mechanical work to its heat terms.

In my calculations, I have taken Po = 2116.3 pounds as the standard atmospheric pressure on the square foot, and J = 1395.846 foot pounds.

Equation (A) gives us a means of calculating either specific heat if we know the other, and also the ratio kp

$\frac{kp}{kv} = y$ a very important quantity in thermodynamics, and also in the study of explosive energy.

Applying equation (A) to hydrogen, in which V_0 , the specific volume of unit mass 1 pound is equal to 178.827 cubic feet we find $k_p = 3.41514$, when k_v is taken as 2.422, and
 $\frac{k_p}{k_v}$

the ratio $\frac{k_p}{k_v} = y$ is equal to 1.410049. This ratio is the same for all diatomic gases. It is usually taken as 1.41.

Another useful element in our calculations is B , the ratio of the whole energy of a gas to its Kinetic energy. According to the Kinetic theory of gases, the molecules are in rapid motion, which is augmented by a rise in temperature. When a gas confined at constant volume receives a certain amount of heat, the increase in its energy may be taken as the dynamical equivalent of the heat. All of this energy (except in monatomic gases) does not take the Kinetic form, or that due to the motion of the molecules as entities. A part takes the form of Internal energy, or that due to the motion of the parts of the molecules with reference to their respective centres of mass. There is a constant conversion of one form into the other, due to collision and exchange of energy between the molecules, but in a perfect gas the relation between them tends to a constant value at all temperatures.

We saw that the Kinetic energy E_k in any state is expressed by $E_k = \frac{3}{2} PV$, the total energy E of the gas or gases is therefore $E = \frac{2}{3} BPV$.

The fraction of the energy which takes the form of Internal energy is larger as the molecule is the more complicated. All gases having the same number of atoms to the molecule have the same ratio between the two energies. The ratio of
 $\frac{k_p}{k_v}$

the specific heats $\frac{k_p}{k_v} = y$ is also dependent upon the number of atoms in the molecule. For a monatomic gas this ratio is $1 \frac{2}{3}$.

For all gases except monatomic the relations which these ratios bear to each other, and to the number of atoms in the molecule, are given in the following equations—

$$y = 1 + \frac{0.41}{\frac{1}{2}N} \quad B = \frac{2}{3(y - 1)}$$

Hence $B = \frac{2}{3(y - 1)}$ in which N is the number of atoms in
the molecule.

These ratios can be computed not only for a single gas, but for any given mixture of gases, such as the products of an explosive. In this case the specific heats are mean or average quantities, and N is the average number of atoms to the molecule.

The experimental determination of the specific heats of gases is very difficult. We owe the most reliable measures to the skill of Regnault, who determined the specific heat at constant pressure of various permanent gases. The most interest-

ing method of getting the ratio of the specific heats — $\frac{k_p}{k_v}$

is from the velocity of sound in the gas. This is based upon the Laplace formula, in which the velocity is shown to be proportional to the product of this ratio, and the square root of the pressure divided by the density. The practical method is due to Kundt—a long glass tube filled with the gas also contains lycopodium dust, or very fine sand. By creating sustained sound waves in the tube of a definite note or pitch, the wave length, which is proportional to the velocity, is defined by the disposition of the dust which gathers at the nodes. The velocity can be compared with the corresponding velocity in

air, for which $\frac{k_p}{k_v} = 1.41$. It was in this way that mercury

vapour was shown to have the ratio 1.666 by Kundt and Warburg, and more recently Argon and Helium were declared to be monatomic on the same ground.

Dissociation and Lack of Temperature Scale.—One of the stumbling blocks in the theory of explosive energy is dissociation of the gaseous products by heat. When an explosive is fired in a closed vessel, and an attempt is made to measure the maximum temperature attained, the actual temperature as determined by the rough means at our command (we have no scale that can be relied upon) is found to be much lower than the theoretical or that which we compute from the heat of decomposition (which we can measure accurately), and the mean normal specific heat of the products. The French school of experimenters, of which the great Berthelot was the head, generally get over the difficulty by supposing that the specific heats of the gases increase with the temperature, and even empiric formulas have been proposed to calculate the actual temperatures. There is a better explanation—viz., dissociation of the products by heat. Practically it makes little difference so far as the actual temperature is concerned, whether the heat is rendered latent in this way, or by an increasing absorbing capacity in the products due to increase of specific heat, but from the point of view of theory one explanation strikes at its root while the other is in accordance with it.

Beyond a few hundred degrees centigrade we have no scale of temperature that is authentic. The air thermometer, through a limited range, has been proved very correct by Joule and Thompson (afterwards Lord Kelvin), by an appeal to thermodynamical principles, which are independent of the properties of any particular substance. The melting points of the refractory metals, such as gold, iron, platinum, etc, which have been used to determine the temperature of fired gunpowder and other explosives, are merely uncertain guesses. Thus the melting point of platinum varies according to different authorities from 1460 to 2534 degrees C.

In the Journal of the American Chemical Society, I published, some 15 years ago, a short paper, entitled, "Argon—an Ideal Thermometrical Substance." Air is composed of two diatomic gases, and theoretically it is subject at high temperature to thermolysis or dissociation by heat. Argon, according to the Kinetic theory, is a monatomic gas, and not subject to this.

If some skilled experimentalist would take this gas and construct a thermometer of it, its expansion under constant pressure, or increment of pressure at constant volume, would give us a scale of temperature that would be absolutely authentic if the Kinetic theory can be relied upon. The Kinetic theory is only a working hypothesis to explain the behaviour of matter in the gaseous state. I have taken it as one of the guides in my study. In this I have been following in the footsteps of such men as Joule, Kelvin, Maxwell and Clausius. I shall take up the subject of Dissociation, or Thermolysis by heat, at a later stage. To consider it in detail now would interrupt the continuity of the treatment of energy.

In the next chapter I propose to give some calculations as to the available energy of several explosives.

CHAPTER VI.

Available Energy or Maximum Work.

The Available Energy of an Explosive.—Diagram for Nitro-glycerin.—Tables.—Available Energy as Affected by Dissociation.—Diagram for Nitro-glycerin.

The Available Energy of an Explosive.—This is the part of the total energy which theoretically can be converted into external mechanical work. So long as the explosive is confined to constant volume no work in this sense is done. To study the available energy, let us conceive an initial state in which the energy is fully developed, and then suppose the gases to expand without gain or loss of heat as such till the pressure is reduced to that of the atmosphere. This is the maximum work which the products expanding from the given initial state can do under terrestrial conditions. The efficiency of the explosive is—

$$\frac{W}{E}$$

, in which W is the available energy or maximum work,
 E

and E is the total energy or potential. The efficiency calculated to the heat is $\frac{W}{J_h}$, in which J_h is the dynamical equivalent of the heat.

The work of adiabatic expansion may be calculated in several different ways. One is by integrating between limits a differential expression for the work— Pdv . A simple method is supplied by the equation—

$$(1) \quad W = kvJ (T' - T'')$$

in which T' is the initial, and T'' is the final absolute temperature, and kv the mean specific heat

of the gas or gaseous mixture. The initial energy is $kvJT'$, the final energy is $kvJT''$, and the work is $\frac{h}{kv}$ the difference between them. $T' = 273^\circ + \frac{h}{kv}$.

T'' the final absolute temperature is obtained from the relation $\frac{T}{p^{\frac{y-1}{y}}} = \text{constant}$, whence $T'' = T' \left(\frac{p''}{p'} \right)^{\frac{y-1}{y}}$, in which $y = \frac{kp}{k'p}$

$\frac{p''}{p'}$ is the ratio of the final to the initial pressure. If we take these pressures in atmospheres ($p'' = 1$) and suppose the products in the initial state to be confined to their specific volume, p' the initial pressure is equal to $\frac{273}{T'}$, and we have therefore

$$T'' = T' \left(\frac{273}{T'} \right)^{\frac{y-1}{y}} \quad \text{and} \quad (2) \quad W = kvJ \left\{ \frac{273}{T'} \left(\frac{273}{T'} \right)^{\frac{y-1}{y}} \right\}$$

We have another expression for the work as the difference between the initial and final energies. The Kinetic energy in any state is equal numerically to $\frac{3}{2}$ of the rectangle of the pressure and volume. B being the ratio of the whole energy to this energy, the total energy will be $\frac{3}{2}Bpv$. From which we have (3) $W = \frac{3}{2}B(p'v' - p''v'')$.

v'' is easily obtained, since $p^y = \text{constant}$ in adiabatic expansion. In this formula W being in foot-pounds, p' and p'' are expressed in pounds, v' and v'' in cubic feet.

In chapter V. I showed how the ratio y and B could be obtained from the number of atoms to the molecule of the gas—or average number to the molecule in a gaseous mixture.

We now give some of the elements in the calculation for nitro-glycerin. The data obtained from the chemical equation of metamorphosis are as follows:—

227 British criths give 14.50 cubic feet.

1 pound gives 11.423 cubic feet = V' the specific volume.
 $H = 336,550$ heat units.

$$h = \frac{H}{227} = 1482.6 \text{ heat units.}$$

Kv — total for 227 units = 48.44 (using 2.422 as the atomic heat of hydrogen).

$$kv \text{ mean} = \frac{48.44}{227} = 0.21339.$$

$$t \text{ rise in temp.} = \frac{336.550}{48.44} = 6947^{\circ}.77.$$

$$T' \text{ the initial absolute temp.} = t + 273^{\circ} = \frac{7220^{\circ}.77}{7220.77}.$$

$$P' \text{ initial pressure in atmospheres} = \frac{273}{273} = 26.4497.$$

$$p' \text{ initial pressure in pounds} = P' \times 2116.3 = 55975.5.$$

$$kp \text{ mean} = 0.276823.$$

$$kp$$

$$\frac{1}{kv} = y = 1.29725.$$

$$B = \frac{2}{3(y-1)} = 2.2427.$$

Computing the work first by equation (2) $W = KvJ$

$$T' - T' \left(\frac{273}{T} \right)^{\frac{y-1}{y}} \text{ in which } \frac{y-1}{y} = 0.229156, \text{ we have}$$

$$T'' = T' \left(\frac{273}{T} \right)^{\frac{v-1}{v}} = 3409^{\circ}.0 \text{ the final temp., and } W = 1,135,385 \text{ foot-pounds.}$$

By formula (3) we have $W = \frac{3}{2} B (p'v' - p''v'')$, in

which $p' = 55975.5$, $v' = 11.423$ cubic feet, $p'' = 2116.3$ pounds, we obtain v'' from $p'v'^y = p''v''^y$.

$v'' = 142.64$ cubic feet, the final volume.

Initial or total energy $\frac{3}{2} B p'v' = 2,150,836$ foot-pounds.

Final energy $\frac{3}{2} B p''v'' = 1,015,433$ foot-pounds.

Difference or work $W = 1,135,403$ foot-pounds.

The difference between the two calculations for the value of W is 18 foot-pounds.

The mechanical equivalent J_h of the heat = 2,069,480 foot-pounds.

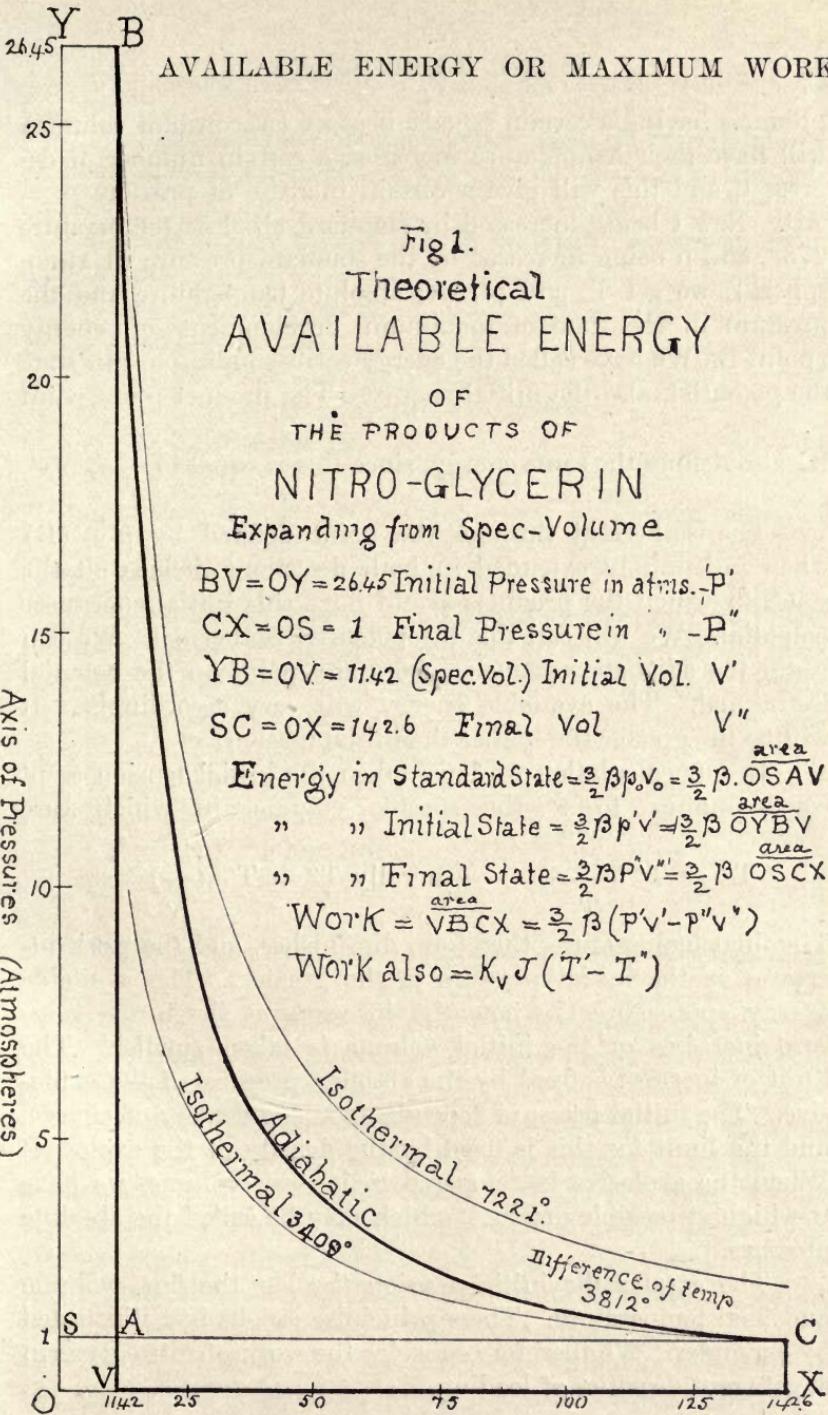
The efficiency calculated to the heat = 54.86 per cent.

Calculated to the potential or total energy = 52.79 per cent.

Diagram for Nitro-glycerin.—We have illustrated the available energy of nitro-glycerin under the condition of expansion of the products from their specific volume by a diagram (see Fig. 1). The work during adiabatic expansion equal to the available energy under the conditions, is represented by the area enclosed in heavy lines VBCX. The diagram is made self-explanatory.

It must be kept in mind that this calculation of available energy is strictly theoretical, even dissociation of the products being ignored.

So far, in computing the work, we suppose the adiabatic expansion to start from the state represented by $p'v'$ (see point B in the diagram), v' being the specific volume of the products. To make the diagram clear, we may first suppose the products to possess this volume in the standard state (point A), and that the heat h is applied to them. Then, by the laws of gases, the



products having a certain specific heat k_v (at constant volume) will have their temperature increased a certain number of degrees t , and this will give a certain increase of pressure $p = AB$. Now t being increased by standard absolute temperature 273° , and p being increased by the standard pressure (1 atmosphere), we get T' and p' , the absolute temperature and the pressure in the state of maximum development of energy (point B. We have called the energy corresponding to this state the potential, also the initial energy. The product $p'v'$ (point

3

B) also defines the same energy, since this is equal to $\frac{1}{2}Bp'v'$.

2

The isothermal through the point defined by $p'v'(B)$ when indefinitely extended in both directions defines all the states in which the products would have this initial energy or potential. We will call this the potential isothermal. We can begin the adiabatic expansion from any point on the potential isothermal. The available energy will vary accordingly. It will be the greater the higher the initial tension.

In our calculation we have taken the initial tension as p' corresponding to v' the specific volume, in which case

$$T'' = T' \left(\frac{273}{T} \right)^{\frac{v-1}{y}} \quad \text{generally } T'' = T' \left(\frac{p''}{p'} \right)^{\frac{v-1}{y}}$$

The final temperature, therefore, diminishes, and the work increases as the initial pressure is the greater. The available energy approaches the potential in value as the initial pressure increases or the initial volume is taken smaller. The limit of increase is fixed by the absolute pressure of the explosive. The initial pressure depends upon the density of charge, and the limit for this is fixed by the density of the explosive. When the explosive is detonated in its own volume, we have the highest possible pressure, which may be called the absolute pressure.

The greater the initial tension the less the final volume and final temperature. These principles can be best illustrated by examples. We therefore consider the work of nitro-glycerin at different densities of loading.

The figures already obtained apply when the initial volume of the adiabatic expansion is the specific volume of the products.

Making similar calculations for adiabatic expansion from unit volume, we have—

$$p' = 639,409 \text{ pounds.}$$

$$v' = 1 \text{ cubic foot.}$$

$$T' = 7220^{\circ}.77 \text{ (this is constant).}$$

$$p'' = 2116.3 \text{ pounds (this is constant).}$$

$$v'' = 82.76 \text{ cubic feet.}$$

$$T'' = 1951^{\circ} \quad T' - T''$$

$$\text{Available energy } W = \frac{T' - T''}{T'} = 73 \text{ per cent. of}$$

potential.

For the initial state of confinement of the products to the volume occupied by the explosive itself giving the absolute pressure (since 100 pounds of nitro-glycerin occupy very exactly one cubic foot), we have—

$$P' = 63,940,900 \text{ pounds.}$$

$$V' = 0.01 \text{ cubic foot.}$$

T' and P'' the same as before.

$$V'' = 28.41 \text{ cubic feet.}$$

$$T'' = 680^{\circ}.$$

$$T' - T''$$

$$\text{Available energy } W = \frac{T' - T''}{T'} = 90.6 \text{ per cent. of}$$

potential. We see from this that the theoretical limit for W which corresponds to the initial absolute pressure is about 91 per cent. of the potential.

The accompanying tables give the available energies of six explosives, considered under three conditions of initial confinement, viz., at the specific volume of the products, at unit density of loading ($V' = 1$), and at absolute density. The mass of explosive considered in each case is one pound. Table No. 1 gives the elements of the calculations, potential, initial temperature, mean specific heat of the products, the ratios y and B and the density of the explosive, which in this sense is the number of pounds occupying one cubic foot. The other

tables give the initial pressure, the initial volume, the final temperature, final volume, final energy, available energy or work done, also the efficiency calculated to the potential $\frac{W}{E}$.

The fourth table also gives the efficiency calculated to the heat $\frac{W}{E}$.

Jh

Table I.—Elements of the Calculation.

Explosive.	E Poten- tial in ft. lbs.	T' Poten- tial temp.	kv Mean Spec.	y — kp	B E kv	D Density of Explosive—lbs. in cub. ft.
1. Nitro-glycerin . . .	2151	7221°	0.21339	1.297	2,2425	100
2. Gun-cotton	1463	4666°	0.22461	1.340	1,958	68.75
3. Picrate Am. Mixture	1484	4094°	0.25969	1.302	2,206	70
4. Am. Nit. Mixt., No. 1	1333	3568°	0.26755	1.302	2,206	62.5
5. Am. Nit. Mixt., No. 2	960	2611°	0.26326	1.328	2,032	62.5
6. Mercury Fulminate..	518	6018°	0.61660	1.454	1,469	276.0

Notes in regard to Composition of Explosives.

2. Gun-cotton.—This is compressed military gun-cotton, taken as $C_{24}H_{29}N_{11}O_{42}$ (13.47 per cent. of N.).

3. Picrate Am. Mixture.—This contains 72.2 parts Ammonium Nitrate, and 27.8 parts Ammonium Picrate.

4. Am. Nit. Mixture, No. 1.—7 parts amorphous carbon (charcoal), and 93 parts ammonium nitrate.

5. Am. Nit. Mixture, No. 2.—13 parts amorphous carbon (charcoal), and 87 parts ammonium nitrate.

Table II.—Available Energy at Specific Volume.

Explosive.	P' Initial pressure in pounds.	V' Initial vol. in cubic feet.	T'' Final temp.	V''' Final vol. cubic feet.	E'' Final energy in 1000 foot. feet.	W Avail- able in 1000 foot. lbs.	W E effici- ency. lbs. ft. lbs.
1 Nitro-glycerin	55975	11.42	3409°	142.64	1015	1135	52.8
2. Guncotton	36172	13.77	2269°	114.44	711	752	51.3
3. Pic. Am. Mixture..	31735	14.13	2184°	113.03	792	692	46.6
4. Am. Nit. Mix., No.1	27661	14.56	1965°	104.80	740	593	44.9
5. Am. Nit. Mix., No. 2	20241	15.55	1495°	85.15	549	410	42.7
6. Mercury Fulminate	46651	5.04	2292°	42.29	197	321	61.9

AVAILABLE ENERGY OR MAXIMUM WORK. 57

 Table III.—Available Energy at Unit Volume— $V' = \text{unity}$ —1 cubic foot.
 $P' \text{ in } 1000 \text{ lb.}$

1.	N.G.	639.4	1	1951°	82.76	581.1	1570	73.0
2.	G.C.	498.0	1	1166°	58.80	365.5	1097	75.0
3.	Pic. Am. Mixture .	448.4	1	1178°	61.14	428.2	1055	71.1
4.	Am. Nit. Mixt., No. 1	402.6	1	1055°	56.29	394.3	938	70.4
5.	Am. Nit. Mixt., No. 2	314.8	1	759°	43.23	278.9	671	70.9
6.	Merc. Fulm.	235.0	1	1384°	25.53	119.1	399	77.0

 Table IV.—Available Energy at Absolute Density— $V' = \frac{1}{D}$.

P' in 1000 lbs.	V' in cubic feet.	T''	V''	E''	D	W	W	
					1000			
					ft. lbs.			
1. N.G.	63941	0.01	680°	28.41	202	1948	90.6	94.1
2. G.C.	34239	0.0145	398°	20.08	125	1338	91.4	97.1
3. Pic. Am. Mix.	31386	0.0143	441°	22.81	160	1324	89.2	95.7
4. Am. Nit. Mix., No. 1 . . .	25164	0.016	404°	21.56	151	1182	88.7	96.4
5. Am. Nit. Mix., No. 2 . . .	19673	0.016	273°.2	15.56	100	859	89.5	100.0
6. Merc Fulm.	64860	0.00362	{ 239°	4.41	21	497	96.0	100.5
			{ 273°*	3.31	23	494	95.5	100.

*In this case $P'' = 3222$ instead of 2116.3 pounds.

Though based entirely upon a theoretical consideration of the subject, these tables are both interesting and instructive.

To roughly summarise the results, we can say for each high explosive considered that, ignoring dissociation, the available energy when it is detonated at specific volume is about 50 per cent.; at unit density of loading about 70 per cent., while the absolute available energy is about 90 per cent. of the total energy or potential.

The first condition is theoretical. The second—one pound detonated in a cubic foot of space, is very light charging. The third condition—one pound confined to its own volume, is always approached, and often reached in practical work. Hereafter, in referring to the available energy, unless otherwise specified, we shall consider this the condition of confinement.

The list of explosives is selected to give as great a range to the elements as possible—thus the total energy of mercury

fulminate is less than one-fourth that of nitro-glycerin. Its absolute pressure (the greatest of all explosives) is $3\frac{1}{4}$ times that of No. 5—the Am. Nit. Mixture No. 2, while its specific volume is less than one-third of that of No. 5, and its density is $4\frac{1}{2}$ times as great.

Mercury fulminate excels all other explosives in efficiency under the three conditions. It owes this partly to the simplicity of its products, but chiefly to their great initial tension.

It will be noticed that in the last table (No. IV.), there are two separate calculations for this explosive. We have already stated the general law that the available energy is limited by the isobaric of the atmosphere, and not by the standard isothermal, 273° . Generally in adiabatic expansion, the pressure of the products reaches an equilibrium with the pressure of the surrounding medium (2116.3 pounds on the sq. foot) before their temperature is reduced to the absolute temperature of the medium 273° . If we assume that the expansion continues to be strictly adiabatic (for instance, that a non-conducting substance separates the products from the medium), the general law is correct in every case. It therefore appears that under this condition mercury fulminate is capable of cooling its products below the standard temperature of the atmosphere. In this, it appears to be unique. However, it would be too much to say no other explosive possesses this power, since one of the others in the table, No. 5—the Nit. Am. Mixture No. 2, all but reaches this temperature. These two explosives present, in some respects, a decided contrast, one having the greatest, the other the least specific volume in the table. These two are the most efficient in converting heat into work, each giving 100 per cent.

Ignoring dissociation, it appears that all high explosives are capable of converting from 94 to 100 per cent. of the heat into work, so that they do not differ much in this regard. There is a law of compensation here which is easy of comprehension. The efficiency, other things being equal, is the greater as the specific volume is larger and the products simpler. The efficiency is also increased by a higher initial tension. As a general rule complex products, while lessening the efficiency

according to the first consideration, increase it according to the second by giving greater heat, and consequently greater initial tension.

Comparing the final volumes V'' (Table IV.) with specific volumes V' (Table II.), it will be noticed that nitro-glycerin nearly trebles the specific volume of its products before their pressure is reduced to that of the atmosphere. Guncotton adds 50 per cent. only to the specific volume of its products. The ammonium nitrate mixture No. 2 just reaches its specific volume, while the fulminate falls notably short of this amount of expansion. These figures help to explain the different actions of various explosives. An explosive with a high initial tension, which yields up its available energy within narrow limits of expansion, is essentially intense and shattering in its effects. If the action is intensified by a rapid rate of detonation, we get the characteristics of a fulminate. Fulminate of mercury strikes a short but intense blow. Its high initial tension is chiefly due to its great density. Its potential is small. Nitro-glycerin combines immense energy, a high initial tension with great length of stroke. Guncotton is very intense (more so than appears from the table, on account of its great speed of detonation). Its energy is great, and its stroke only moderately long.

We pause to note that the maximum pressure is given by mercury fulminate, nearly 65 million pounds on the square foot, or 450,000 pounds on the square inch—about 30,600 atmospheres. That of nitro-glycerin is, theoretically, nearly as high, but this must be diminished something like one-half by dissociation. The other is approximately correct; dissociation will not lessen it more than, say, 10 per cent. as a guess.

Available Energy as Affected by Dissociation.—So far we have ignored dissociation in considering the available energy. The general effect of dissociation will be to lessen this so that the figures we have obtained are too high. Nevertheless, these figures as they stand have a value as a limit. For at least one explosive in the list, the fulminate, they may be taken as approximately correct. When this is closely confined it probably converts at least 90 per cent. of its heat into work. No

other explosive yields up its energy so completely and within such narrow limits of expansion. Its energy, however, is very small.

Generally dissociation will have two opposite tendencies—first, by lessening the initial tension, it will reduce the available energy, but it will simplify the products, and thus render them more efficient in converting a given amount of energy into work. The latter effect will not counterbalance the first, however, and in all cases the available energy will be reduced by dissociation. The expansion can no longer be considered adiabatic, since the heat, or part of it (that rendered latent by dissociation), will be received during the expansion and cooling of the products.

If, however, we could know the initial state (defined on a diagram by a point having certain co-ordinates pressure and volume), and could draw the adiabatic for this initial state, then the work so defined would be an inferior limit for the available energy just as that calculated (or determined graphically) for the potential initial state would be a superior limit. The real curve defining the states through which the products passed in reaching an equilibrium with the atmosphere, would lie, for the greater part of its course, between these two adiabatics. However, in the lower part of its course it will intersect the potential adiabatic, and give a greater final volume than pertains to the latter.

We can state the case in the form of a general equation. Suppose, for simplicity, that in the final state of the expansion the products are those given in the chemical equation of metamorphosis—that is, dissociation is absent in this state. This is highly probable from the values of the final temperatures given in Table 4, and although these do not govern the case, the real temperatures being higher, the supposition is still justifiable.

Let E be the potential.

E' the initial active energy developed.

Then $E - E' = L'$, in which L' is the energy rendered latent by dissociation in the initial state—which energy is also the sum of the energies received by the products during ex-

pansion. Let E'' be the final energy of the products in the expansion.

$$\text{Then } E'' = E' + L' - W; \\ \text{Or } E'' + W = E.$$

That is, if dissociation is absent in the final state of the expansion, the potential is still developed, and this is divided between the work done and the final energy.

The expansion being no longer adiabatic, we cannot calculate the final energy or the work. The general effect of dissociation will be to increase the final energy at the expense of the work—more work will be done at lower tension and less

3
at higher. In the expression for the final energy, $\frac{B}{2} p''v''$,

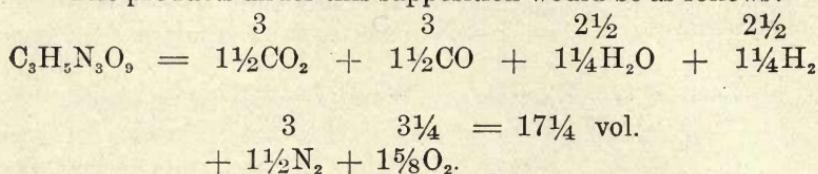
the final pressure is fixed at one atmosphere; B is peculiar to the products of the explosive (dissociation by hypothesis being absent in the final state), the final energy can therefore only be increased by increasing the final volume v'' .

Again in the expression for the final energy, $J. kv T''$, $J.$ is a constant, and kv is peculiar to the products (being independent of dissociation unless monatomic products are present, which is unlikely in the final state*); the final energy, as dependent upon these elements, can only be increased by increasing the final temperatures.

We illustrate these principles by making a calculation for the adiabatic expansion of nitro-glycerin, assuming that in the initial state (absolute density of loading 1.6; V' being equal to 0.01 cubic feet), there is a dissociation of one-half the triatomic products (given in the normal equation of metamorphosis) into diatomic products. Of course there is no authority for this particular amount of dissociation. It is taken merely as an illustration, and also great enough, as we think, to furnish an inferior limit for the work.

*Mercury Fulminate is a rare exception—one of its products, Mercury Vapor, is monatomic.

The products under this supposition would be as follows:—



Now supposing there is an adiabatic expansion from this initial dissociated state, the elements of the calculation would be as follow:—

The heat developed per unit of mass, $h' = 716.2$.

The heat energy, $Jh' = 999,692$ ft. lbs.

The initial energy, $E' = 1,081,008$ ft. lbs.

The heat energy rendered latent by dissociation, $L' = 1,069,788$ ft. lbs.

The spec. vol. of the products = 13.39 cubic feet.

The corresponding pressure = 28,134 pounds.

The initial temperature T' (absolute) = 3629°.

The rectangle of pressure and volume $pv = 382,317$.

$\frac{kp}{kv}$

The ratio $\frac{kp}{kv} = y = 1.3537$.

The ratio $B = 1.885$.

Making the calculation for the adiabatic expansion from absolute density, we have—

P'	T''	V''	E''	W	W	W	W
1000 pounds.	final temp.	final vol.	final engy. 1000ft. lbs.	work 1000 ft lbs.	— E'	— Jh'	— E
38,232	280°	13.96	88.4	997	92.3	99.8	46.3

The calculation shows that the efficiency calculated either to the active initial heat or to the initial energy developed, has been slightly increased. This is owing to the simplification of the products (note change in y and B as compared with former tables). But the efficiency calculated to the potential is found to be lessened nearly one-half (46 against 91 per cent.).

The work under this supposition is about one million foot-

pounds, and this may be considered as an inferior limit to the available energy.

This calculation takes no account of the energy rendered latent by dissociation. By hypothesis this energy is given out or developed during the expansion of the products, so that the expansion is not adiabatic, and the work defined by the adiabatic curve through the point representing the initial dissociated state is certainly too small.

If, however, we assume what is almost self-evident, that the initial state gives the maximum development of energy—then the isothermal through the point which represents the initial state forms a superior limit for the expansion and the actual curve of expansion lies between the adiabatic and isothermal through this point.

We may imagine various forms for the actual curve. For instance, that it coincides with the isothermal for part of its course.

Then the only work done would be by conversion of the latent heat as fast as it developed as active energy into work. The limit of conversion should be about 1,070,000 foot-pounds (see value of L' above). When this was reached the actual curve would fall away from the isothermal and take the course of an adiabatic.

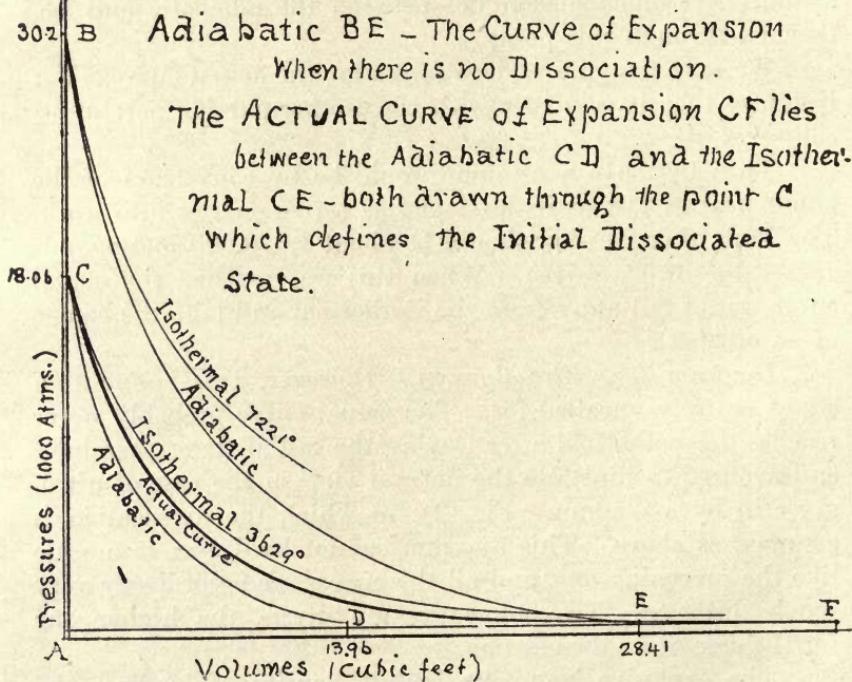
Diagram for Nitro-glycerin.—However, this supposition seems entirely uncalled for. The actual curve probably never reaches the isothermal after leaving the initial state. We have endeavoured to illustrate the natural view in the case of nitro-glycerin by a diagram (Fig. 2), in which the dissociation is assumed as above. This diagram cannot be drawn to a scale like the preceding one, and all the curves are accordingly very much distorted. Two adiabatics are given, the higher one for the case of no dissociation.

The explosive being at absolute density of loading, the volume in the initial states in both cases is 0.01 cubic feet. The work corresponding to each curve is the area included between the curve, its extreme ordinates and the axis of volumes. The work corresponding to the adiabatic BE is 91 per cent. of the potential. That corresponding to the adiabatic CD is 46

per cent. of the potential. That of the actual curve is between these limits, and can only be guessed at.

It will be noticed that the actual curve CF lies below the isothermal CE throughout its course, and also that it intersects the greater adiabatic BE, and gives a final volume AF

Fig. 2.
Diagram to Illustrate
The ABSOLUTE WORK of NITRO-GLYCERIN
as affected by DISSOCIATION



considerably greater than that corresponding to the adiabatic's final volume AE.

We repeat once more that the assumption in regard to the amount and character of the dissociation is simply used as an illustration. However, if at some future day we are able to

calculate the dissociation in the initial state, the principles enunciated will apply.

The general view we take of dissociation is that it is determined by the nature of the products—the more complex these are, the greater the dissociation. It is also a question of temperature, and not of pressure—being the same for different densities of loading. Whatever may be the amount of dissociation in the initial state (the amount is measured by the heat rendered latent), both the energy developed and the energy rendered latent are at a maximum in this state—that is, both the active and latent energies diminish during the expansion of the products. The law of diminution is something between that of adiabatic and isothermal expansion.

The general effect of dissociation will be to lower the absolute work or available energy of an explosive by increasing the final temperature and the final volume. It will diminish the shattering effect of an explosive and lengthen its reach. In many cases it will increase the useful work—a point to be noticed later.

While it will modify the characteristics of an explosive deduced from the theoretical study, it will not obliterate them.

There is one point which is not well covered by our theory. We were careful to say that the laws of gases can only apply to the products of an explosive when there is equilibrium or uniform distribution of energy among them. In the initial state of tension of a fired explosive, especially one with a high rate of detonation, this condition of equal distribution of energy does not obtain, and we cannot say that the laws of gases hold good for the system. The action exerted on the walls of a containing vessel is not in the strict sense a pressure. We even know that the action is not equal in all directions. It is held by some students that a greater part of the energy takes the Kinetic form than called for by the laws of gases. If this were so, it would tend to offset the effect of dissociation in lessening the initial tension, and in reducing the percentage of the potential, which can be converted into work. This idea has been carried to the limit of supposing that in the first instants of detonation, the dissociation is complete, leaving all

the products reduced to atoms, in which case the whole energy would be Kinetic. Nothing could be more unphilosophical than such a supposition. Where does the energy come from if not from the union of the atoms? If the molecules are all dissociated, there is no active energy to be considered. In regard to the Kinetic energy being in excess of that required by theory, we can, with just as much, if not more, reason, suppose the internal energy greater than theory calls for. The simplest way to get over the difficulty is to suppose that the mean of the actions in all directions is equal to the pressure, which we could deduce if the energy were uniformly distributed. The state of uniform distribution is reached in any case in a very short space of time if the products remain in one body. While the theory is unable to cover the condition of irregular distribution of the energy, this condition is not a serious obstacle to its useful application.

CHAPTER VII.

Useful Work.

Useful Work.—General Principle for Hard Rock.—Bank Blasting.—Classification of Explosives.—Tests for Energy.—Mortar.—Quinan Crusher Gauge.—Work in the Mortar.—Effect of Dissociation.—Effect of Rates of Detonation.

Useful Work.—This is defined in chapter VI. as that portion of the available energy of an explosive which can be applied to a special object. It is equal to the available energy less the dynamical equivalent of the heat lost as such by communication to other bodies, and the energy expended in useless work. It is therefore dependent in a general way upon the available energy. From our calculations of available energy or maximum work we reach the conclusion which, however, is hardly of more than theoretical interest, that it increases as the atmospheric pressure is lower.

If we designate the potential or total energy of the explosive by E, the available energy by W_a , and the final energy, when the pressure of the products has reached an equilibrium with that of the atmosphere, by E_f , our theory of available energy may be expressed as follows:—

$$W_a = E - E_f$$

This simple formula applies whether dissociation be considered or not. If we take it into consideration, E_f is larger, and W_a smaller, than the theoretical values. If dissociation be absent in the final state of the products, E_f represents both the active and the total energies of the products, these quantities being the same. If dissociation be present in the final state, then E_f represents the total energy—that is the sum of the active and latent energies.

In the following discussion we will suppose W_a to have the practical value due to dissociation. The available energy or maximum work has been calculated under a condition which cannot be practically realised, namely, that no energy is lost by communication of heat as such to surrounding bodies, during the expansion of the products. If we denote the energy so lost by Jh' , this gives us one element to be subtracted from the available energy. Making this allowance, we have

$$W = W_a - Jh'.$$

This value W is realised in one form or another of mechanical work.

In regard to the loss of heat as such, we can arrive at some idea of its magnitude by the following course of reasoning. Other things being equal, it will be greater as the temperature of the products is the higher, and we might therefore conclude that explosives, which depend chiefly for their energy upon high temperatures (class 1) are subject to a greater loss than explosives which are energetic chiefly by reason of the great volume of their products (class 2); but it will not do to jump at conclusions. There are several other factors concerned in the loss of heat, the chief ones being the conductivity of the surrounding bodies, and the time of contact. In detonating explosives, this time is usually very short. For instance, when nitro-glycerin is detonated in contact with wood, the wood is generally reduced to minute splinters, but there is rarely the slightest sign of charring, though this only requires a temperature of about 350° C. Moreover, there is a law of compensation which justifies us in believing that in the ordinary case the loss is not only small, but that it is something like equal for different explosives. Explosives of class 1 having high temperatures are generally much quicker than those of class 2.

Without great error, we can therefore neglect the loss of heat, and write—

$$W = W_a.$$

A part of this is not generally useful; for instance, the portion expended in displacing large masses of the surrounding air is ordinarily wasted.

If we denote by U the useful energy, and by W_x the energy expended in all other kinds of work not useful in the particular case, we have

$$U = Wa - Wx.$$

We are compelled to treat the subject in this general way because the useful work of an explosive is a chameleon-like thing, which varies with every different application. What is useful work in one case is useless work in another. The noise made by an explosive is generally its most useless effect, but in firing salutes this is the only useful work accomplished by it.

Sometimes in hard rock, when the explosive is not intense enough, or is not properly stemmed, it will blow out the tamping and expend the greater part of its energy uselessly through the bore-hole. But this action is the useful one if we desire to give motion to a projectile.

Mechanical work, like every other form of energy, is made up of two factors—intensity and capacity. The intensity factor is the resistance—the capacity factor is the path. The first determines whether or not the action takes place—the second measures its extent. By offering a resistance greater than the intensity of the explosive in every direction but one, we may compel it to perform its work chiefly in that direction. This is the cardinal principle of gun construction, and is also utilised to a certain extent in blasting. The blaster locates his charge, if possible, so that the line of least resistance is not through the tamping, but in some other direction, so as to get a maximum disruption and displacement of rock.

If the resistance has great intensity, a very small path may involve great work—work being the product of the two. Intense explosives develop intense resistances, and consequently tend to short paths in mechanical work.

We have already shown in discussing available energy that each explosive has its peculiar characteristics in regard to intensity and path, and also how for any explosive one factor can be increased only at the expense of the other; as the initial tension is higher, the final volume of the products is lessened.

The selection of an explosive is mainly determined by

the intensity of the resistance to be overcome—Hard, tough rock demands an intense explosive.

General Principle for Hard Rock.—In regard to useful work in hard rock, a general principle can be deducted from our formula.

$$U = Wa - Wx.$$

We see that generally U is the greater, as Wa , the available energy is the greater. For every explosive Wa increases as the initial tension is higher or as the density of charge increases. Therefore the careful blaster compresses his charge into the smallest possible compass in the bottom of the bore-hole, and secures it with a tamping packed tight and hard to the mouth of the hole. Experience has taught him that “the better the tamping the better the blast.”

This is the ordinary case of blasting in hard rock. The object is to expend the available energy on the rock itself—that is, to perform as much work locally, and at as high resistance as possible. The work expended outside of the sphere of the blast, either in projecting fragments of rock or in giving motion to the atmosphere, is wasted energy.

In this special case, the shorter the path (this corresponds to the final volume of the products in our previous discussion) the less energy is wasted. This path is shortened by increasing the initial tension.

Bank Blasting.—There are cases, however, in which it is necessary for the gases to work over a longer path. Although the available energy is lessened thereby, the useful work is increased. In bank blasting, where large masses of earth and loose rock or gravel are to be broken up and displaced, if the charge expends its energy at high tension in the interior of the mass, we will get a small expansion of the gases, and the mass will not be broken up nor moved as desired, and the blast will be a failure.

For this sort of blasting intense explosives are not desirable. Blasting powder (especially that made with sodium nitrate base) has been used with good effect, but still better is a class of detonating explosives that has been specially developed for the work. These explosives, which are peculiar to the United

States of America, are essentially low dynamites, usually containing about 5 per cent. of nitro-glycerin.

When moderate charges are to be used, as in the progressive destruction of a bank of earth, the drilling is done from the top. A chamber at the bottom of the drill hole is made by firing a small charge of dynamite without tamping. This chamber is filled loosely with the low grade explosive.

When a large mass of material is to be moved or broken up by a single great blast, a tunnel is run into the hill, and a T is cut at the end to hold the charge. Generally speaking, close confinement of the charge itself, or great density of loading, is not necessary—in fact, would injure the efficiency of the blast. The tunnel, however, is carefully closed with bags of sand or by some other effective method. In this way the products retain sufficient final energy to tear their way through the mass and break it up. Each particular case, however, requires special treatment, depending upon the object aimed at. This method of blasting (which found formerly an extensive field in connection with hydraulic mining), as well as the class of explosives most suitable for it, may be considered the invention of Egbert Judson, an early American friend of Alfred Nobel's, and one of the great industrial pioneers of California.

One is somewhat at a loss to explain the great efficiency in this sort of work of these low grade detonating explosives as compared with their energy equivalents in blasting powders. I think it is due to the fact that the initial explosion is accompanied by a shock which tends to break and fissure the ground, making paths for the disrupting action of the gases. These low grades have a velocity of detonation of from 3000 to 5000 ft. a second. They are at their best in loose rock, shales and the like, cemented gravel, or a mixture of earth and rock. They do not work well in wet or mucky ground, or in hard homogeneous rock.

Classification of Explosives.—We see that the useful work varies in kind in different forms of blasting. In order to treat the subject to advantage, we must make a broad distinction between explosives that work best at high intensity, with short paths—that is, with relatively small expansion of volume, and

those which are intended to work at a lower intensity—and with relatively large expansion of volume. The simplest division we can make is into—

- (1) High grades.
- (2) Low grades.

There is no absolute distinction between these classes, for they run into each other in what may be called the medium grades—nitro-glycerin, blasting gelatin, gun-cotton, gelignites, and both high grade gelatin dynamites and dynamites of the Lig-Dyn or Keiselguhr type belong to the first class. The 50 and 40 per cent. Lig-Dyns belong to the medium grades, and all below the latter may be classed as low grades.

Tests for Energy.—It is a necessity to the manufacturer to have some means of rating explosives. One of his tests should, as far as possible, give the useful work of the explosive under what may be called the average conditions of blasting. In this sense the best general test that I know of is the mortar.

Mortar.—This, as I use it, is a short, heavy gun, bedded in a thick block of concrete, at an angle of elevation of 45° . The shot being heavy, and its velocity low, the resistance of the air may be neglected, and the trajectory be considered a parabola. According to a principle of mechanics, the work done in foot pounds is $\frac{1}{2} M.R.$, in which M is the mass of the shot in pounds, and R the range in feet. I do not contend that the range in the mortar determines the relative value of the explosive in every kind of blasting. I regard it, however, as a good all round test in a general sense.

Quinan Crusher Gauge.—When it is desired to test explosives with reference to their use in hard rock, I prefer the crusher gauge described in "Cutter and Crusher Gauges for Explosives," published in the Proceedings of the U.S. Naval Institute, No. 64, and also described in Guttmann's "Explosives."

This consists of a piston, 4in. in diameter, moving between upright guides, and containing a small cavity in the upper end for the charge. A shot weighing about 35lb., with a fuse hole directly over the charge, is placed upon the piston, and the latter rests upon a cylindrical lead plug, which is crushed by the piston when the charge is fired. The compressions of the

lead plug are translated into foot-pounds according to a dynamic scale—a scale made by crushing similar lead plugs by a falling weight.

In the mortar the gases act upon the shot till the latter clears the muzzle. Owing to the construction of the "crusher gauge," there is almost an immediate release of the gases, which act only for an instant on the piston. The gases therefore do their work on the lead, while they are at very high tension. In the mortar they have a chance to expand somewhat, and work down to a lower tension.

Notwithstanding this difference of action, the indications of the two instruments in rating explosions agree more nearly than one might anticipate. Considering explosives of the same nature—that is, mixtures of the same ingredients in different proportions—no case has fallen under my observation in which the rank of any two explosives is reversed by the tests.

In a general way the mortar is more favourable to lower grades, and the crusher gauge to the higher. If the relative rank of two explosives is reversed in the two instruments, we can draw certain conclusions as to their intensity. For instance, the useful work in the mortar of the Picrate mixtures (72.2 Am. Nit. and 27.8 Am. Picrate—see tables in chapter VI.), compared with the guncotton is 235 : 226.

In the crusher gauge the gun-cotton takes precedence, the relative numbers being 370 : 350.

This means that the gun-cotton does relatively more work at high tension. It is therefore better suited to hard rock, while for average conditions the picrate mixture would do more useful work.

Work in the Mortar.—I have thought it instructive to make a comparison for different explosives between the actual work done in the mortar and the theoretical energy available under the conditions of firing. It is necessary to consider the theoretical available energy—dissociation being ignored, as otherwise we cannot make the calculation. The sketch, Fig. 3, shows the mortar and its chamber, in which the charge is placed. The diameter of the bore is 4.4in. The weight or mass (which is the better term) of the shot is 33.7 pounds. The

uniform charge of explosive used is 70 grains, or 1-100 of a pound. The capacity of the little chamber was originally 210 grains of water, giving a density of loading of 0.333. The chamber at the time of the experiments was somewhat enlarged. I have taken its capacity at 233.3 grains of water, giving a density of loading of 0.3. The density of loading is based upon a convenient expression, for it proposed by the French experimenters—viz., the mass of the charge in grammes divided by the capacity of the vessel (or space in which the charge is detonated) expressed in cubic centimetres.

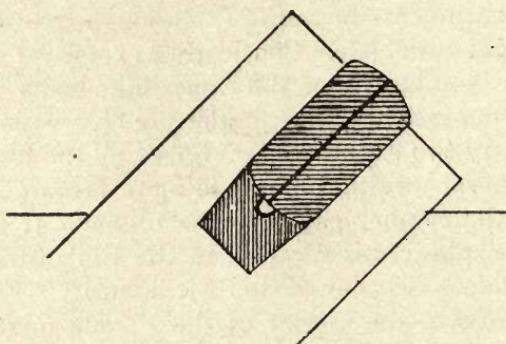


Fig. 3.—Mortar.

The body of the mortar is of cast iron. The chamber is formed in a block of hard steel. This block is tapered, and when first used must be driven into its seat by firing heavy charges. A wedge to remove the block when the chamber is worn out is not shown. This wedge passes entirely through the body of the mortar just below the seat of the chamber block.

In order to make the calculation, I assume that the charge is completely detonated in the chamber before the shot begins to move, also that the gases act usefully in giving energy to the shot till the latter just clears the muzzle. Therefore in the adiabatic expansion the initial volume will be .000533 cubic feet. This is the volume of the chamber. The final volume of the gases will be 0.0785 cubic feet. This is the capacity of both chamber and bore. We now propose to calculate the energy which is theoretically available between these limits—that is, the work of adiabatic expansion between this initial

and final volume for several explosives, and to compare the results with the actual or useful work in each case. The methods of making the calculations have already been explained.

We select 4 explosives from the list already given in chapter VI. For the Ammonium Nitrate mixtures No. 1 and No. 2 we have substituted a mixture, No. 3, consisting of Ammonium Nitrate about 87 per cent., and a soft paraffine about 13 per cent. This latter gave by ultimate analysis very nearly the composition $C_{14}H_{30}$, so that it may be considered vaseline.

In regard to the equation of metamorphosis, as the products are very deficient in oxygen, there is some question about their exact composition; but by applying certain principles (which cannot be cited here), I have been able to get an equation which I have no doubt is substantially correct.

The heat h for unit of mass = 550 heat units.

The specific volume V (for 1 pound) = 18.495 cubic feet.

kv . the mean specific heat of the products = 0.30714.

kp

$\frac{—}{kv} = y = 1.3344$.

kv

$B = 1.9937$.

E potential = 884,710 foot-pounds (for 1 pound).

N, the average No. atoms to the molecule = 2,452.

This explosive is a remarkable instance of low heat and great specific volume. It is not a practicable explosive, however, as it stands. It will not transmit the detonating impulse in mass, but a small quantity of it can be fully exploded in the mortar or crusher gauge, and its detonation on a working scale can be insured by the addition of a small or large percentage of nitro-glycerin. Explosives of this kind are well known in the United States, where their advantages are fully appreciated. Their rates of detonation are lower than the Lig-Dyns (see summary of Dr. Comey's paper, chapter II.).

As the composition given produces a large percentage of carbon monoxide (CO) in detonation, it would be objectionable in deep mining, unless the ventilation were very active. However, an extreme case of the type is chosen to bring out certain principles.

HIGH EXPLOSIVES.

Comparison of Different Explosives.

Table 5.—Theoretical Energy Available in the Mortar.—Charge, 70 grains (1-100lb.).—Density of charge, 0.3.—Initial Vol. $V' = 0.000533$ cubic feet.—Final Vol. $V'' = 0.0785$ cubic feet.

Explosive.	Initial Energy, ft.-lbs.	Initial Temp., °	Initial Pressure (1000lbs.)	Final Temp., °	Final Press. (lbs.)	Final En'yg Av'ble, ft.-lbs.	Energy Ef	Wa	Wa Prcfge.
Nitro-glycerin ..	21,508	7221°	11,989	1637°	18,468	4877	16,631	77	
Guncotton	14,630	4666°	9,338	853°	11,598	2675	11,955	82	
Pic. Am. Mixt. ..	14,840	4094°	8,407	906°	12,640	3284	11,556	78	
Am. Nit. Mix., No. 3	8,847	2064°	5,551	385°	6,816	1648	7,199	81	

This table shows that roughly about 80 per cent. of the total energy of each explosive is theoretically available under these conditions in the mortar, so that the available energies preserve nearly the same relations to each other as the total energies bear to each other.

Taking the available energy of nitro-glycerin as 100, we have the following numbers:—

Relative available energies in the mortar—

Nitro-glycerin	100
Gun-cotton	72
Pic. Am. Mixt.	69.5
Am. Nit. Mixt., No. 3	43

The actual ranges of the different explosions, with a closely fitting shot, weighing 33.7 pounds, were as follows:—

Nitro-glycerin	290 feet
Gun-cotton	226 ,
Pic. Am. Mixt.	235 ,
Am. Nit. Mixt., No. 3	230 ,

Calling the work (or range to which it is proportional) of nitro-glycerin 100, we have—

Relative Useful Work.

Nitro-glycerin	100
Gun-cotton	78
Pic. Am. Mixt.	81
Am. Nit. Mixt., No. 3	79

Some further comparisons are shown in the following table, No. 6. The useful work in foot-pounds is computed from the formula $U = \frac{1}{2}M.R$ — M, being the weight of the shot

33.7 pounds, and R the range in feet. We give the percentage values of U , E and W_a , taking that of nitro-glycerin as 100:—

This table shows that the useful work compared with both the potential and with the energy theoretically available in the mortar is greatest for the ammonium nitrate mixture, and least for nitro-glycerin.

Relation of Intensity and Capacity of Factors to Useful Work.—In this discussion we shall use the term useful work or useful energy in a broad sense, viz., as that portion of the energy which can be realised in ordinary mechanical work. *We do not include the work expended in very minute paths, and great intensity, such as the erosion or graving of metals, or the reduction of hard rock to powder.* The work done in the mortar is a type of useful work in this general sense, though the term as we intend it also includes work done at much higher tension.

We can draw certain general conclusions from our tables as follows—There is no direct relation between the maximum work or theoretical available energy and the useful work. In

U
Indeed, in a general way, the useful work efficiency —

E
is greater as the available work W_a is less. As we saw before, the available energy for a given potential is greater, as the intensity factor of the latter is the greater, whereas the useful energy is greater as the capacity factor is the greater. Maxi-
 W_a

mum work efficiency — implies a high initial tension, and a
E

sudden running down of the energy. Useful work efficiency implies a more sustained effort. Mercury fulminate exceeds all other explosives in maximum work efficiency. Its useful efficiency is very low.

The elements relating to “intensity” are temperature, pressure, density of loading, and rate of detonation. These form one class. Rate of detonation we have yet to consider.

The elements relating to “capacity” are the specific volume and specific heat. Temperature is the most general of the first

HIGH EXPLOSIVES.

elements. It is independent of all the others of this class, being even independent of mass. The pressure is independent of mass for the same density of loading. The "capacity" elements increase directly with the mass. The intensity and capacity factors of the energy can be readily distinguished when the latter is expressed directly in mechanical units or in terms of PV. P is the intensity and V the capacity factor.

Table 6.—Useful Work in the Mortar—Charge, 70 grains (1-100 pound); weight of shot, 33.7 pounds.

Explosive.	U.		E.		Wa.		U	
	Useful work, foot-pounds.	Initial energy N.G.	or potential. foot- pounds.	100.	Theoretical. foot- pounds.	N.G.	per cent.	per cent.
	$\frac{1}{2}MR.$	100.						
Nitro-glycerin	4886	100	21,508	100	18,631	100	23	29
Gun-cotton	3808	78	14,630	68	11,955	72	26	32
Pic. Am. Mixture	3980	81	14,840	69	11,556	69.5	27	34
Am. Nit. Mixt., No. 3..	3875	79	8,847	41	7,199	43	44	54

The most general expressions for the energy is obtained by translating its thermal value into mechanical units as J.T.kv. In this T is the intensity factor, and Jkv is the capacity factor. J is constant for the same mass—kv is peculiar to the products, and increases with their specific volume.

The relation between the intensity and capacity factors of the potential determines the general character of the explosive in regard to useful work efficiency. Comparing these factors for the different explosives in the tables, we see that the Ammonium Nitrate mixture presents a decided contrast to the nitro-glycerin and gun-cotton. The initial temperature is

3

less than — of that of nitro-glycerin, while the capacity of fac-
10

tor kv is nearly 50 per cent. greater. Compared with gun-cotton, the temperature is considerably less than half, while the capacity factor is 40 per cent. greater.

There are certain effects involved in the mortar experiments which our theory cannot take into account. One of these is the influence upon the useful work of the rate of decom-

position. There is probably a certain rate which is most favourable to the useful work on the shot. Nearly all high explosives when fired with a detonating fuse exceed this useful rate, and suffer in consequence a loss of work. In regard to this loss, gun-cotton suffers most, and the Ammonium Nitrate mixture least.

Effect of Dissociation.—This is brought out clearly by a study of the tables. Dissociation increases with the initial temperature, and the complexity of the products. For the explosives given in the tables, it is the greatest for nitro-glycerin, and the least for the ammonium nitrate mixture. The

U

apparent low value — for nitro-glycerin is chiefly due to the
Wa

effect of dissociation. Wa in the tables is a theoretical value, which ignores dissociation, that is, the explosives are credited with an available energy larger than the active energy developed would justify. This explains the poor showing that the nitro-glycerin makes in regard to useful energy efficiency. The actual tension of the products is lowered by the heat rendered latent, and undoubtedly the gases escape from the mortar with a part of the energy in the potential or latent state. The loss from this source amounts to something for all the explosives, but is much greater for nitro-glycerin than the others. The others suffer losses in the following order:—Picrate mixture, gun-cotton and ammonium nitrate mixtures. As the last consists mostly of diatomic products, with a low initial temperature, the loss is probably very small.

In the case of explosives like nitro-glycerin with complex products, and a theoretical high initial temperature, we believe that the useful work in the sense we are giving the term, is in all cases increased by dissociation. The influence of dissociation is to moderate the “fulminate effect,” by which we mean a very high initial tension, with a sudden running down of the energy. Dissociation lengthens the stroke, and increases the useful energy.

Effect of Rate of Detonation on Useful Work.—This subject is debatable ground. In a general sense, a high rate of

detonation has the opposite effect to dissociation. The first has a tendency to favour the "fulminate effect," while the second lessens it.

The principles we have deduced for nitro-glycerin (which is not regarded nowadays as a practical explosive in mining) hold good for blasting gelatine and high-grade gelatins and dynamite. Blasting gelatin is nearly the energy equivalent of nitro-glycerin, being slightly superior to it. Gelignite, gelatin dynamites, and high-grade dynamites are inferior to it in energy, but belong to the same class.

The rates of detonation of these explosives, however, vary greatly. Blasting gelatin may be said to have normally a high rate, the dynamites a medium rate, and the gelignites a low rate. In the case of the gelatinous explosives, the matter is complicated by physical condition, as well as by the degree of confinement and the strength of the detonator. The gelatinous explosives vary in velocity of detonation from about 6000 to 28,000 feet a second.

In these notes, I have persistently advocated good confinement, and strong detonators, especially for gelatinous explosives. This is on account of their peculiar nature. Under conditions that are slightly unfavourable they are subject both to a breaking off or a dying out of the detonating wave, so that special precautions should be taken to insure their complete detonation. This does not make me, however, an advocate of the highest rate of detonation, though I admit that there is this argument in its favour, or in favour of the physical condition of the explosive most conducive to it. A high rate is probably less liable to an interruption or dying out of the wave. Another question is bound up with the main one. How does the velocity of detonation affect the chemical metamorphosis? We know that very low rates of detonation (due either to insensitiveness of the explosive, non-confinement, or inadequate detonators), even in explosives containing a sufficiency of oxygen, lead to low orders of explosion, and to incomplete oxidation of the products—some oxygen unites with the nitrogen, leaving the carbon deficient, and producing the poisonous carbon monoxide—but we think this condition per-

tains to abnormally low rates. The question should be made the subject of a special investigation, but our opinion seems to be justified, because experiments in the Bichel and Golaz bombs usually show a normal metamorphosis, although the small quantities of explosive are detonated at a very moderate rate, if we can judge from the circumstances of the firing.

Assuming that a rate of, say, 7000 or 8000ft. a second, a velocity rarely exceeded by gelignite, is sufficient to give normal chemical metamorphosis, the most interesting question is this—is the useful work in the average case of hard rock blasting increased or lessened by a high rate? If it is increased, what is the limit of velocity which will give the best effect? We know that a gelignite with a velocity of 7000ft. seems to do good work, but so does a blasting gelatin with a rate three times as great. Possibly, within wide limits, the useful work is not seriously affected. Our belief is that the useful work of gelignite in hard rock can be increased by increasing its rate of detonation—even to doubling it, which can be readily done with a small primer of Lig-Dyn. But we do not believe in making either gelignite or blasting gelatin so sensitive that they can be detonated at a high rate without confinement. I believe that blasting gelatin was at its best in the days of Alfred Nobel, and his immediate successors, so far as its efficiency in very hard rock was concerned. As a guess, it had a velocity of detonation not extending 18,000ft. a second, when it was well confined, and was fired with a strong detonator. The soft sensitive blasting gelatin that has become the standard in Australia probably has the maximum rate of 27 or 28,000ft. in the bore-hole. In spite of dissociation (which we have always with us), I think there is in such a case a certain degree of the “fulminate effect,” which does too much molecular work on the rock—work of high intensity and short paths—grinding it to dust—an expenditure of energy that could be more usefully employed in disrupting and displacing it. This opinion is based upon my experience and observation, but both are liable to error, and the opinion must be taken for what it is worth. Absolute proof is wanting.

Economy in Blasting.—The useful energy of an explosive is measured by its rock-getting capacity—the number of cubic

feet or tons of rock that a pound of it will remove. In nearly all cases the stronger of two explosives, other things being equal, will show a better return, but this does not necessarily make it the more economical. The measure of economy is the cost of the unit of useful energy in the particular case. In very hard refractory rock, the ideal explosive is blasting gelatin. Under such conditions, practical trials always show it to be the most economical explosive that can be used. But all sorts of rock are encountered in mining, and to meet the needs of the industry there should be low and medium, as well as high, grades. It is wasteful in more senses than one, to use high grade gelatinous explosives in soft rock. Not only are they unnecessarily expensive, but the confinement is not good, and great care is requisite to insure their complete detonation. One is always hearing of unexploded cartridges being found in the debris. This is so common that it is looked upon as a matter of course, and they are searched for as a part of the routine work.

The employment of these explosives in all kinds of rock without reference to its resistance, tends to make the miners careless and wasteful. Blasting is an art, which is never learned by the man who always uses a surplus of energy to accomplish his task, while the one who uses a grade adjusted to the resistance naturally acquires the skill necessary to make it do its work. He learns to take advantage of the lay of the ground, to study the planes of cleavage, and to get all the help he can from a proper location of his bore-holes. He gauges carefully the depth of his holes, their burden, and the necessary charge. He never puts in a "pinched hole"—that is, one that can only break in the general direction of the tamping, if it is possible to avoid it. A skilled blaster in an extended trial will make an inferior explosive remove more rock per pound than one 20 per cent. stronger in the hands of a poor blaster, trained in the school of surplus explosive energy.

Conditions in Australia.—It is strange that in so enterprising a country as Australia there should be an almost utter lack of the medium and lower grades of explosives for general mining. The gelatinous explosives, the lowest grade of which is the ordinary gelignite, practically monopolise the

field. It is true that lower grades are found in coal mining, but this seems to be for a special reason. High temperatures must be avoided in "safety explosives," and the grades seem to be lowered for this reason, and not to adjust the energy to the work. Where the coal mines are not "fiery," I have in several instances found gelignite used even for coal getting.

In the matter of grades, the United States presents a strong contrast to Australia. At the large dynamite factory which I managed years ago in California, the average grade manufactured contained 42.5 per cent. of nitro-glycerin. In Australia, the average grade consumed must be about double this. In America, the chief aim is to produce the unit of useful work at the lowest possible cost. If we understand useful energy to apply to the average conditions in mining, then this unit can be more cheaply produced in the form of Lig-Dyn, or "straight dynamite" (Dr. Comey's designation) than in gelatinous explosives. In California, the amount of blasting gelatin produced and consumed was insignificant—such is the power of fashion. Each country, America and Australia, could have well taken a lesson from the other. If Australia would make more use of the medium and lower grades, and America would use more blasting gelatin for the special case of very refractory rock, economy would accrue in both instances. As I left California 12 years ago, I am not competent to speak of the conditions prevailing there at present. In Australia, they are far from ideal.

CHAPTER VIII.

Strength of Explosives.

Tests for Strength.—**Density of Loading.**—**Pressure of Gunpowder.**—Rumford, Piobert, Rodman, Nobel and Abel.—**Pressure of High Explosives.**—Berthelot, Sarran and Vicille.—**Testing Devices.**—Guttmann's Pressure Gauge.—Trauzl Lead Block.—Bichel's Pressure Gauge.

Tests for Strength.—“Strength” is a general indefinite term relating to the power of an explosive, or its capacity for doing work. Since the days of Count Rumford, who made the first notable attempt to determine the absolute pressure of gunpowder fired in a closed vessel, investigators have been indefatigable in devising apparatus for indicating the strength of explosives. These efforts have had a very happy termination in the case of gunpowder and other explosives of the same class, such as Brown or Cocao, and smokeless powders, used as propellants in gunnery. Not only has the absolute pressure, when fired in closed vessels, been determined with accuracy, but the pressure developed behind the shot in practical firing is now a matter of daily measure. The theory of the crusher gauge, as applied to gunnery, has been well worked out. A small copper cylinder is compressed or shortened by the action of the gases upon a piston, and the amount of this compression indicates the maximum pressure. The calibration of the copper cylinders, to get a scale of pressures, is extremely simple. The crushing has only to be done slowly—that is, by an increasing weight or other force, acting without velocity, in order to obtain a direct relation between the compression and the corresponding pressure. In such a case the resistance developed, and the pressure exerted, are in equilibrio throughout the path of the deforming force.

When the crusher gauge was applied to detonating explosives at high densities of charge, with a view to determining the pressure, unexpected difficulties and complications arose, and the problem of thus measuring the pressure has remained unsolved to this day. One reason for this difficulty lies in the nature of the two classes of explosives—the slow or gunpowder class, which explode by combustion, and the quick explosives, which explode by detonation. The rate or velocity of decomposition is so different in the two cases as to leave a gulf between them. The first class evolve thin gases relatively slowly, so that, in a closed vessel, when precautions are taken to prevent the movement of the gas as a whole, the energy may be considered uniformly distributed throughout the space. The intensity factor of the kinetic energy is the pressure, and this has the same value throughout. In detonating explosives, this condition cannot be taken as existing at the moment of maximum development of the energy—that is, the latter cannot be assumed to be uniformly distributed. The utmost we can assume, and even this is somewhat doubtful, is that the mean intensity of action in every possible direction—if we could determine it—would be equal to what we calculate from theoretical data as the pressure. The question is one of almost infinitely small periods of time. If we suppose the products to retain their heat for the fraction of a second there, by the properties of gases, the energy will uniformly distribute itself; but between the instant of maximum energy and this state there is a gap which we cannot bridge with certainty.

Density of Loading.—With these qualifications in mind we can lay down some principles in regard to pressure, which are generally accepted. The pressure of an explosive fired in a closed vessel, allowance being made for the cooling effect of the walls of the vessel, varies with the amount of explosive used in proportion to the volume available for its products. The ratio between these quantities is called the “density of charge or loading.” The products of an explosive may be wholly gaseous or partly gaseous and partly solids. For low densities of charging the presence of the latter may be neglected, and the pressure will be directly proportional to the density, in

accordance with Boyle's law. It is reasonable to suppose that for explosives giving only gaseous products, this law— pv constants—extends to the highest densities of loading, but the experimental difficulties are so great that the law has not been verified in the case of high explosives. At very high densities explosives which give partly solid products do not obey the law, owing to the disturbing effect of the presence of these solids.

The ratio expressing the density of loading is the same, no matter what system of units is used, but when French units are employed the definition of density of loading is simply the number of grammes of the explosive divided by the space available, or volume of the vessel, in cubic centimetres.

Several convenient terms are used to denote certain definite pressures. The specific pressure is the pressure when unit mass is detonated in the specific volume of the products—that is, in the volume which these would occupy under standard temperature and pressure, according to Avogadro's law. As these quantities—unit mass and specific volume—bear the same relation to each other in the two systems, British and French, the specific pressure is the same in the two systems.

The pressure at unit density of loading is also the same in the two systems. In the French system this is also the pressure at unit volume—that is, when unit mass is detonated in unit volume; but in the British system the pressure at unit volume is a different and smaller measure, corresponding to one pound detonated in one cubic foot, or a density of loading of about

1

— The pressure at unit volume is called the "force" of the
62.5

explosive. This is numerically equal to $\frac{2}{3}$ of the kinetic energy, and has the same value in the two systems, but is differently expressed, being foot-pounds in the British system, and kilogram-metres, or gram-centimetres in the French, depending upon the unit of mass and volume used.

The absolute pressure is the pressure when the explosive is fired at the maximum density of loading—that is, when the space is quite filled with the explosive. The amount present depends upon the specific gravity of the explosive itself, or the density

which can be given it by compression, and this, again, depends upon its state of aggregation, consistency, plasticity, and other physical qualities. For most industrial explosives the practicable density of loading exceeds unity, varying between this and 1.65. In actual blasting of bore holes the maximum, or absolute density, is generally reached in charging, and the absolute pressure of the explosive is realised if the rock is sufficiently resistant. For gunpowder or blasting powder, the absolute density of loading is generally taken as unity, though it varies slightly, depending upon the granulation and specific gravity.

Pressure of Gunpowder.—*Rumford, Piobert, Rodman, Nobel and Abel.*—Benjamin Thompson, Count Rumford, was the first investigator who undertook in earnest the task of measuring the pressure of fired gunpowder. This was near the close of the 18th century (1797). His plan was simplicity itself. He used a small vertical mortar, or eprouvette, the bore of which was closed by a short close-fitting stopper, upon which rested a heavy weight. The pressure was determined by varying the charge, and noting whether or not the weight was lifted so as to allow the gases to escape. Rumford concluded that the absolute pressure of gunpowder (density of loading about unity) was more than 100,000 atmospheres.

In the early part of the 19th century, General Piobert, a celebrated French authority, made some experiments which satisfied him that Rumford's estimate was much too high. He lowered the figures to about 23,000 atmospheres.

About 1857, General Rodman, of the U.S. Army, worked at the problem, using his cutter gauge, attached to a cast-iron shell, in the centre of which he exploded small charges of gunpowder. He estimated the absolute pressure at about 13,000 atmospheres.

The question was finally settled about 1874, by Captain Nobel and Professor Abel, in their classic researches on "Fired Gunpowder." They used the Nobel crusher gauge, and found for the absolute pressure about 6400 atmospheres, or 42 tons on the square inch, for service gunpowder, and 44 tons for mining or blasting powder. The results of Nobel and Abel, since confirmed by other experimenters, have been generally accepted.

Pressure of High Explosives.—*Berthelot, Sarran and Vicille.*—Shortly after Nobel and Abel finished their work—the second sets of their researches being made in 1878—the French experimenters, Sarran and Vicille, attempted to apply the crusher gauge in determining the pressure of certain high explosives. The results of the first set of experiments, covering a wide range of densities, are given in Berthelot's great work on explosives, an English translation of which, entitled, "Explosions and their Power," is published by Sampson, Low and Company, of London.

The apparatus employed was similar in essentials to that used by Nobel and Abel. It consisted of a cylindrical steel vessel of small capacity (24.3 c.c.), strengthened by steel wire wound round it, under tension. One end of the cylinder was fitted with the firing arrangement, the other carried the crusher gauge, the essential of this being a movable piston, resting upon the copper cylinder, with the needful arrangement for supporting and manipulating both.

The calibration of the copper cylinder was effected by crushing them progressively and slowly in a dynamometer (similar to that used by Nobel and Abel, Rodman, and other ordnance experts), until the compressed cylinder supported without further deformation a given load or pressure. In this way was obtained a relation between the pressure P (Kgms. in the square c.m.), and the corresponding compression, e in millimetres, expressed by the following equation:—

$$(1.) \quad P = 541 + 535e.$$

Berthelot gives an account of Sarran and Vicille's experiments in the light of their latest theories in "Explosives and Their Power." He proceeds as follows:—"This relation being established, how can the resulting indications be applied to experiments? Two limiting cases present themselves:

"(a) The development of the pressure is slow enough, and the mass of the crushing piston small enough to permit of the force of inertia being neglected, and in this case there is practical equilibrium between the pressure developed by the explosive and the resistance of the cylinder. The maxi-

mum pressure is then equal to the force of calibration corresponding to the crushing observed.

"(b) The development of the pressure is so rapid that the displacement of the piston taking place during the development of the maximum pressure may be disregarded, the piston having besides a sufficient mass: in this case the movement of the piston may be regarded as effected under constant pressure from the start, and throughout the whole of its duration. The calculation shows that the value of the pressure is equal to a force of calibration corresponding to half the crushing.

$$(2.) \quad P = \frac{541 + 535}{2}^e$$

Of these two limiting cases so tersely put by Berthelot (a) applies to slow explosives, (b) to quick, or detonating explosives. There can be no dispute as to case (a). It is to the treatment of case (b), quick explosives, that exception must be taken. It will be noticed that the same system of calibration is applied to both classes—that is, it is assumed that the copper cylinder offers the same resistance for the same amount of compression, whether crushed slowly or almost instantaneously. The only difference of interpretation is that in the case of quick explosives, the pressure is assumed constant, and equal not to the maximum, but to the mean copper resistance. This is equivalent to crediting quick-acting explosives with about half the normal pressure for the same amount of copper compression. As we now know that the resistance offered by copper to deformation is greatly increased when the rate of application of the deforming force is very rapid, we think the reasoning of the French experimenters erroneous, and all the pressures obtained from formula (2) much in error, and the conclusions drawn from them equally fallacious.

The experiments of Sarran and Vicille covered several years, and the various results were published from time to time. As in the case of gunpowder, there has been a tendency to reduce the values first published. To illustrate the tendency downwards of these results, we will notice some of the figures published for the absolute pressure of mercury fulminate. The

first result was about 100,000 atmospheres. This was deduced, I think, from the pressure curve, by producing it to the theoretical maximum density of charge, which, of course, was unattainable in practice. The next figure that I recall was 48,000 atmospheres. This prevailed till about 1882, when Sarran and Vicille's new theory of crushing manometers had been fully developed. The latest result is 26,000 atmospheres, but though this agrees approximately with the theory, it does not appear entitled to any more credit than the other. There has been a corresponding decrease in the figures for other explosives, thus guncotton has been reduced from 24,000 to 10,000 atmospheres. In "Explosives and Their Power," both sets of figures are given very frankly by Berthelot. The fact seems to be that the earlier experiments, which were made in great detail, and for quite a series of densities of charge, were based directly upon the system of calibration and interpretation of compressions, which apply properly to gunpowder. The results were accepted until the knowledge of explosives, and the theory of explosive energy, had advanced far enough to enable Berthelot to make the theoretical calculations, from which it appeared that these results in many cases were far in excess of the theoretical pressures. A reform was felt to be necessary, and this led to the special investigation by Sarran and Vicille in 1882.

The principal feature of this investigation was an attempt to determine the duration of the crushing, by a delicate chronoscope, capable of measuring $\frac{3}{10\,000}$ of a second, which was operated in connection with the movements of the crushing piston.

In the experiments upon gunpowder, by changing the granulation, the time of action was made to vary through a range of more than 1 to 50, and without changing the crushing effect. Formula (1) is therefore applicable to this agent under all conditions.

Powdered potassium picrate decomposed so rapidly that no appreciable value could be observed for the time of crushing expressed in $\frac{1}{10\,000}$ of a second. With powdered guncotton—density of charge 0.20—the time was also inappreciable, al-

though the mass of the piston was varied from 42.7 to 727 grammes.

Dynamite, the detonation being produced by fulminate, decomposed more slowly than guncotton, but more quickly than gunpowder, and the time varied with the mass of the piston. To quote Berthelot:

" It therefore supplies an intermediate case, in which the discussion of the measurements is more delicate. By employing pistons of medium weight, and even light pistons, it is very difficult to attain the lower limit, (1) at least with a certainty comparable to that of the experiments relative to the preceding substances. On the other hand, towards the opposite limit, (2)

t^*

the ratio — may be neglected by giving the piston a mass to

of 4kgms.; the crushing was then nearly double that obtained with pistons weighing 3.8grms. and 6.9grms. Hence it can be seen that the two limiting cases have been realised with dynamite, as also the intermediate cases, by modifying the mass of the piston.

" The maximum pressure for a piston of 4kgms. has been found equal to 2413kgms. per square c.m., for the density of charge 0.30. With a piston of mean weight, that is, weighing only 59.7grms., the density of charge being still 0.30, dynamite and picrate give the same crushing (1985kgms.); however, the maximum pressures are very different."

I draw the following conclusions from the experiments on dynamite:—With the detonator employed it was possible, by increasing the weight of the piston, to make the explosive work so slowly that it fell into the gunpowder class, but in that case formula (1) should have been applied, and not formula (2), as appears to have been done. When a very light piston was used the action was rapid enough to develop the higher form of copper resistance, or something approximating thereto, therefore the compression was small. With a heavy piston, on the

* t is the time of crushing by the explosive, t_0 the time in the calibrating machine.

contrary, the lower form of resistance was developed, giving, consequently, a greater pressure.

Berthelot remarks: "It is clear from the above with what precaution the crusher must be employed to measure the maximum pressure of explosives." I agree with him in this. Moreover, I go further. I believe that it is impossible to measure with the crusher gauge the *pressure* of high explosives, which are quick enough to develop the higher form of copper resistance.

I hold in the case of quick-acting explosives, that the deformation of the copper is a dynamic effect, and a record of work. I have gone into the subject quite fully in the paper "Cutter and Crusher Gauges for Explosives," Proc. U.S. Naval Inst., 64, and need not discuss it here in detail. In my opinion it is impossible to get in this way an absolute value for the pressure of detonating explosives. The compression of the copper is a record of work, and it can be properly interpreted only by the dynamic system of calibration—a scale made by a blow such as that of a falling weight. The crushings obtained by the French experimenters were not records of pressure, but dynamic effects, largely dependent on the rate of detonation of the explosive, of which the pressure is theoretically independent. To get values for the pressure reasonably consistent with theory, they were led to adopt a system of calibration which credited detonating explosives with about half the normal pressure corresponding to the compression, although it has been proved since that the resistance of the copper increases instead of decreasing with the quickness of action.

"Explosives and Their Power" is a mine of valuable data in regard to explosives, but the student who expects to gain from it accurate ideas of the pressures of high explosives, as determined by practical experiment, will be disappointed. He will generally find, at least for each important explosive, two sets of widely different values for the pressure. The set belonging to the old series is generally given in detail for densities varying from 0.1 to 0.7 or thereabouts. The new set is more limited, generally for one density only, sometimes for two, as 0.2 or

0.3. The new figures are always considerably less than the old, as may be inferred by comparing formulas (1) and (2).

Berthelot seems to attach importance to both sets of figures, although if one is right the other must be wrong. The general result is a tangle, from which it is hopeless to draw safe conclusions, although Berthelot indulges in hypothesis based sometimes on one set and sometimes on the other set of figures.

It is very easy thus to criticise the work of eminent investigators in the light of knowledge which neither they nor anybody else possessed at the time. The law of copper resistance to stress (as well as that of other metals) was first discovered and formulated by Prof. R. H. Thurston, a member of the celebrated "U.S. Board for Testing Metals," and the report of the Board had not been published when Sarran and Vicille made their experiments. Allowance must also be made for the circumstances under which Berthelot wrote his great book; his stupendous industry in nearly every field of chemical research, and the enormous labour which would have been involved in re-writing it, and making it a consistent whole. It must also be remembered that these great men were pioneers in the study of high explosives, and that the theory was still in its infancy. Even the distinction between detonation and combustion was not clearly recognised, and some of their errors arose from confounding the two phenomena. For instance, guncotton and the picrate were fired with a red-hot wire instead of a detonator, and although fulminate was used for dynamite, the quantity was insufficient, resulting (as we know from the record) in a low order of explosion and low velocity of detonation.

Notwithstanding these circumstances, the French school of investigation accomplished a great deal to advance the study of High Explosives, and the student owes them a great debt of obligation.

Testing Devices.—In testing the strength of high explosives, the difficulty of determining the pressure has led many to rely upon tests more nearly related to the useful energy or work which the explosive is capable of doing. The mortar described in a previous chapter is perhaps the oldest of such devices. The useful work is directly proportional to the range.

The Quinan crusher gauge, also already noticed, is another. The indication of the energy is the compression of a lead plug, and this is translated into foot-pounds of work by comparison with a scale of compressions made by a falling weight, under the assumption that the rate of application of the force of deformation is approximately the same in the two cases, and develops the same resistance in the lead plug.

Guttmann's Pressure Gauge.—One of the earliest gauges designed for testing both classes of explosives is that proposed by Oscar Guttmann (see Guttmann's "Explosives"). It consists of a hollow steel cylinder fitted with a piston at each end, the pistons bearing upon lead plugs. The charge is fired in the middle of the cylinder, through a side tube, and the gases force the pistons outward, compressing the plugs into conical recesses in the capped ends of the cylinder. The special feature of the apparatus is that the firing device locks the tube so that the explosion takes place in a closed space, and even slow explosives like gunpowder give a good record. The apparatus is well designed for its special object, which is to make the record independent of the quickness or velocity of explosion. However, there is a difficulty in translating the deformations of the lead plugs into any units relating to the energy. If a system of calibration be used appropriate to the slower explosives like gunpowder, we have no assurance that the scale so obtained is applicable to high explosives. In fact, from our knowledge of the properties of lead under stress, we have good reason to think that it is not. Lead flows freely under stress, so freely that General Rodman found it nearly impossible to get a scale of calibration for it suitable for gunnery. Its most marked peculiarity is that the resistance offered to deformation rises rapidly with the rate of application of the deforming force. As there is an enormous difference in the rate of application in the two classes of explosives, this property of lead renders it unsuitable as a gauge for both classes in the same apparatus. The Guttmann gauge is a valuable aid in testing explosives, but it must always be kept in mind that its indications, which in the case of quick

explosions are records of work, not of pressure, are unduly favourable to the slow explosives.

Trauzl Lead Block.—One of the simplest and widest known tests for high explosives in the Trauzl lead block. According to the specifications adopted by the Fifth International Congress of Applied Chemistry, this consists of a cylindrical lead block 20cm. high, and 20cm. in diameter. It is bored from the top end, with a central charging hole 2cm. in diameter and 12cm. deep. The charge is 10 grammes of explosive. The detonator being placed, the charge is stemmed with sand and clay or plaster of Paris. When the charge is fired a pear-shaped cavity is formed in the interior of the block. The capacity of this is measured in cubic centimetres, by filling it with water from a graduated vessel. If proper precautions are taken in making the lead blocks to secure a uniform quality of lead, and in getting a homogeneous casting, and also in providing a uniform resistance in the stemming of the charge, the test is a valuable one. However, the volume of the explosion cavity, expressed in cubic centimetres, cannot be taken as an accurate comparison of the work done by different explosives. In a general way, the test is relatively more favourable to explosives of great energy and high velocities of detonation. Though the lead offers less resistance to slow acting explosives, these are at a disadvantage, because they will blow out the tamping before the gases have been fully developed, and have had time to expend their energy in expanding the lead. Explosions of the gunpowder class fail for this reason to form a perceptible cavity. Strong explosives are relatively favoured, because the resistance of the lead walls to stretching diminishes as the cavity enlarges. We can therefore say that the Trauzl block test favours unduly strong, quick explosives.

Bichel's Pressure Gauge.—The most notable attempt to determine the pressure of high explosives experimentally has been made recently by C. F. Bichel, managing director of the Carbonite Explosives Company Limited, of Hamburg, a gentleman who has done a great deal to advance both the experimental and theoretical study of explosives. His pressure gauge is an adjunct of

the well-known Bichel explosive bomb, which in its usual form is a hollow steel cylinder, about $31\frac{1}{2}$ in. long, and $19\frac{3}{4}$ in. in exterior diameter—one head secured with heavy steel bolts, being removable. The explosion chamber is about $7\frac{7}{8}$ in. in diameter, and 19 in. deep, so that its capacity when closed is actually 15 litres. The charge to be tested is placed in the chamber on a small wire-work tripod, and fitted with an electric detonator, the wires of which are carried through the walls of the chamber. The chamber is closed at one end with a strong steel cover, lead washers being used to insure a gas-tight joint. An attached air pump enables the operator to get a high vacuum in the explosion chamber before the charge is fired.

The pressure gauge mounted on the top of the cylinder, directly over the charge, is constructed somewhat like the indicator of a steam engine. The gas acts upon a piston held down by the tension of a spring. The upper end of the piston carries a stylus, which traces, during the action of the gases, an undulating curve upon an independent drum mounted upon a vertical axis, and rotated by clock work. The curve, after a few undulations, settles down into a nearly horizontal line, showing the permanent pressure of the products. The height of the first undulation, corresponding to the maximum compression of the spring, indicates the maximum pressure. This initial upward movement, owing to the momentum of the piston, and its connected parts, gives an indication in excess of the true maximum pressure, which excess is the greater for explosives having high rates of detonation. This excess, according to Bichel, rarely exceeds 2 or 3 per cent. The undulations of the curve are steeper in proportion to the rate of detonation. The author states that with practice the height indicating the true maximum pressure can be located with accuracy, but he does not show exactly how this is done.

The maximum pressures found in the explosion chamber are lower than they should be on account of the cooling effect of the surrounding surfaces. Herr Bichel eliminates this effect of surface, and arrives at the true pressure in the following ingenious way. By using bombs of the same capacity, but of

different diameters and lengths, he is able to increase the superficial area surrounding the charge, while keeping the volume of the chamber and density of loading constant. For instance, the 15-litre bomb is given three different surface areas—3600, 6600 and 7600 square cm. By plotting a diagram, in which the surface areas are abscissas, and the observed pressures are ordinates, and connecting the summits of the latter, a straight line inclined to the axis is obtained, which produced to the axis of ordinates (the line of o surface) gives the true pressure for the density of charge, the surface influence being eliminated. Proceeding in the same way with the pressures in a smaller bomb, which is also given several different surface areas, and by covering a wide range of densities with both bombs, he is able to prove that Boyle's law holds very accurately, through a range of densities, from $1/_{150}$ to $1/_{25}$, provided the cooling effects of surface be eliminated. This is certainly a notable achievement—one which goes far to put the theory of explosives upon a sound footing.

The student of explosives will find a full description of the apparatus in a little book by Herr Bichel, which has been translated into English by Axel Larsen, M.Inst.M.E. The translation is entitled, "Testing Explosives," and is published by Charles Griffin and Company Ltd., London.

In regard to the pressures at very high densities, the author, after giving the demonstration mentioned above, goes on to say: "It may therefore be taken for granted (pending future evidence to the contrary, perhaps through the introduction of stronger apparatus and higher densities) that the pressure obtained with a density of $1/_{150}$, and corrected for surface influence, is directly proportional to those obtained with higher densities."

Taking the corrected pressures for a density of $1/_{150}$ as a basis, he then calculates the absolute pressure of a number of explosives. The figures for the first four explosives in the list

are given below. I have added the third column to show the pressure in atmospheres.

	Highest density of charging.	Pressure kgms. per sq. cm.	Pressure in atmospheres.	Relative pressures.
Gunpowder	1.04	2,917	2,822	1.0
Blasting gelatin	1.63	17,213	16,654	5.9
Kieselguhr dynamite . .	1.58	11,420	11,049	4.0
Gelatin dynamite	1.67	13,878	13,428	4.7

The first thing that strikes the notice in this table is the low absolute pressure given for gunpowder—2822 atmospheres, whereas Nobel and Abel, for nearly the same density of charge (1 instead of 1.04) found about 6400 atmospheres. But this is easily explained. Herr Bichel's calculations do not take into account the solid products, which form more than half the weight of the products. At the density $\frac{1}{150}$ the relative space occupied by these is insignificant, but at the density 1.04 they occupy more than half the available space. If we credit them with taking up about 59 per cent. of the space, which is about right according to the views of various experimenters, we get a very fair agreement between Bichel's result and that of the English authorities.

In regard to the figures for the other explosives, we will revert to them later.

CHAPTER IX.

Theories of Explosion.

Limitation of Theory.—Vortex Action.—Direction of Maximum Action.—Behaviour of Guncotton.—Influence of Detonator.—Anomalies.—Pressure vs. Dynamic Effect.—Effect of Inequality of Action.—Case of Closed Vessels.—Velocities of Molecules.—High Densities of Charge.—Low Densities of Charge.—Bichel's Results.—Emmens' Ballistic Theory.—Sarran's Theory.—Bichel's "Percussive Force."

Limitations of Theory.—I have given, in preceding chapters, a consistent theory of explosive energy—a theory which in its main essentials is approved by all the great authorities. But some of the phenomena of explosion are not well covered by this theory, and other theories have been proposed. Before we consider these it will be well to set forth the natural limitations of our theory, and show wherein it fails. The theory is based upon the laws of gases, and the Kinetic theory of their action. The first condition to make these laws applicable is that the energy must be uniformly distributed throughout the gases. There is grave doubt, to say the least, whether this first condition obtains among the products of a high explosive at the instant of maximum tension. But circumstances must have an influence, and it is well to consider the subject in some detail before arriving at a conclusion.

Berthelot, in relation to the pressures obtained with the crusher gauge, says (see "Explosives and Their Powers"—page 25): "It should be remarked that the measurements thus obtained correspond only to a certain mean of pressures—a mean which is capable of being considerably exceeded at certain points. In reality, the gases suddenly developed by the chemical reaction represent real whirlwinds, in which there exist jets of matter under very different states of compression, and an interior fluctuation."

Vortex Action.—Vortex action probably plays always some part in the movement of explosive gases. At least such an idea might be drawn from certain experiments by Prof. Threlfall, published in the Phil. Mag., 21, 1886.

He fired small glass bulbs filled with mercury fulminate in a tank of water, and watched the phenomena through glass windows. The *debris* of the explosion seemed to be shot out with the rolling motion peculiar to smoke coming out of a chimney. It was projected with great velocity, and came to rest suddenly a few inches from the seat of the explosion. As the projection took a decided direction, experiments were made to determine whether the greatest energy was also exerted in this direction. For this purpose pendulum gauges were used, and making allowance for anomalies these showed that the direction of the maximum explosive effect coincided with the direction in which the *debris* was projected.

The vortical or rolling motion of the *debris* is sometimes seen on a grand scale when a dynamite mill or nitro-glycerin house is blown up. The initial conditions here cause the *debris* to be projected upwards. It is generally shot up straight into the air, forming a conical shaft, which is crowned at the top with wreaths and billows of smoke. The vortex or rolling smoke motion is not clearly observable till the shaft has reached an altitude of several hundred feet, or until it has highly compressed the overlying air. A very beautiful phenomenon of the same nature occurs when a large charge of explosives is fired under water.

Direction of Maximum Action.—The most vital deduction from Prof. Threlfall's experiments is that the direction of maximum effect can be foretold with reasonable certainty if we know all the initial conditions. When small charges are used, the direction of the maximum effect depends on the initial arrangement of surrounding obstacles, and especially on the position of the detonator. The phenomena of factory explosions, and of large submarine mines, show that there is a "line of least resistance" for high explosives as well as for gunpowder—and the direction of this line decides the direction of the maximum effect.

General Abbot (see "Report on Submarine Mines") has shown that even large submarine charges of high explosives sometimes give unequal actions in different horizontal directions, the maximum direction being always upward. This unequal horizontal action is probably to be traced at least in most instances to imperfect centreing of the detonator. In the case of gunpowder, "the line of least resistance" can easily be predetermined by special arrangement. This was also demonstrated by General Abbot. By partially filling a wooden keg with mortar powder, and confining it in place by a wooden partition, he created an air space in one end of the keg. The powder gave a much greater action in the direction of the air space. The pressure in this direction was undoubtedly reinforced by the movement of the gas as a whole.

Rumford, in his experiments on gunpowder, used a small bored eprouvette pointing upwards. The charge occupied the lower part of the bore, the upper part being empty. He therefore got the same reinforced action, and an effect about 16 times the normal. This is undoubtedly the explanation of his exaggerated value for the absolute pressure of gunpowder. Even in General Rodman's experiments this ballistic effect was probably experienced in some degree, and accounted for his high value for the absolute pressure. It was only when this ballistic effect was avoided by placing the charge directly in contact with the crushing piston, or other recording apparatus, that the true pressure of gunpowder was obtained.

Behaviour of Guncotton.—In connection with the ballistic action of explosive gases, some curious effects have been noticed in the behaviour of compressed guncotton. If a block of this explosive be detonated on a wrought iron or steel plate strong enough to resist rupture, an impression will be made upon the plate which is a reproduction of the face of the guncotton block in contact with it. If letters are sunk in the block, corresponding letters will be found *sunk* in the metal plate. Prof. Chas. E. Munroe has studied this phenomenon, and given the only rational explanation of it. By increasing the cavities in the guncotton block, he deepened those in the steel. Finally, by using a block of guncotton with a hole entirely through it, he

succeeded in perforating a corresponding hole in the plate. On account of their great penetrating power, he nick-named these perforated blocks "Rifled Guncotton." Prof. Munroe's explanation is that the effect is chiefly a ballistic one. The hole through the block is a line of least resistance, which also serves to concentrate the action of the molecules. The situation is also favourable to vortex action, and to erosion of the metal.

Influence of Detonator.—The influence of the detonator in giving direction to the maximum effect is well known to practical men. For instance, if we wish to break an iron rail, we set the cartridge upright upon it, and place the detonator in the top end. If we insert the detonator near the bottom, we get a much smaller effect. It is also well known that the effect of a shell charged with high explosive on an armour plate is much greater when the detonating fuse is placed in the base than when it is placed in the point of the shell. This influence of the position of the detonator, or of the starting point of the detonating wave, is easily understood. If we suppose a column of explosive to be undergoing detonation, we note that the successive layers explode as the wave reaches them. At this moment, for a given layer, the molecules are found with an intense pressure, due to the gases of the layer already exploded on one side of them, while in the other direction they find comparative freedom to expand. In a limited sense we can say that the action in the direction of the wave is cumulative.

Anomalies.—Anomalies, however, in the action of high explosives, are sometimes observed, which cannot be explained by reference to this principle. A good illustration is to fire a dynamite cartridge on the top of a wooden stake, around which are driven 8 or 12 shorter stakes, about 2 or 3 ft. from the central one. The effect of the explosion will be to break down the outer stakes, or to "brush" their tops, depending upon the charge. Generally it will be noticed that the effects are unequal on the different stakes, and the inequality cannot be explained by lack of symmetry in locating the detonator, because this would give a general direction to the maximum effect, whereas adjoining stakes may show very different effects. A still better illustration is afforded when a larger quantity of

dynamite explodes in a factory building which is surrounded by a forest of young trees. Outside of a zone, in which the trees are uprooted and utterly destroyed, the damage will usually be found apparently capricious. Lanes of destruction will be seen projecting far into the wood, with radial spaces between, left comparatively unharmed. The explanation usually given is that the globe of heated expanding gas, in driving back and compressing the surrounding envelope of air, breaks through it at certain points, forming "tongues of force," in the path of which the destruction is a maximum.

The phenomena so far noticed have little bearing upon the question of a theory of explosives. A theory implies conditions that are more or less ideal. Such a condition is the confinement of the products of the explosive in a closed vacuous vessel, the walls of which are non-absorbent of heat. No vessel can be made which is strictly non-conducting, but this does not seriously affect the application of the theory.

Pressure vs. Dynamic Effect.—One of the first questions which the student of explosives must face is this: Does the factor of the Kinetic energy, which we call pressure, obtain at the moment of maximum development of energy in the product of a detonating explosive fired in a closed vessel? This question is equivalent to another: Is the action of the exploding products equal in all directions, or, to put it possibly in a simpler way, is the energy uniformly distributed throughout the system? If so, the laws of gases apply no matter what the intensity of the action, and our theory will hold. We have good reason to think that this uniform distribution of energy does not obtain under high densities of charge, so that the technical term "pressure" does not cover the effects developed, but if we adopt the reasonable view that the mean of the actions *in all directions* is dependent upon the energy (which we can calculate) then the theory is still helpful.

Effect of Inequality of Action.—We pause to note that though the theory of explosive energy may be sound, and we may even be able to calculate a value for the energy of the explosive, which cannot be exceeded, yet this inequality of action in different directions may in practice give the explosive a

power apparently in excess of the theoretical. From the very general character of the resistances encountered in nature, it is evident that complete disruption is much more likely to take place when a maximum effect is exerted in some one direction, than if equal effects obtain in all directions. In the first case we may suppose the stress to be concentrated on a point. If disruption occurs at this point, a general smash of the resisting system may follow, whereas if the stress had been uniform over the whole area, the resisting system might have been preserved more or less intact. These considerations can be applied with profit to certain experiments made by the French investigators in bursting shells with high explosives.

Case of Closed Vessels.—With the help of the Kinetic theory of gases, we can make an interesting study of the behaviour of explosive gases in a closed vessel.

The subject naturally falls into several heads:—

- (1.) Firings at high densities of charge.
- (2.) Firings at low densities of charge.
- (3.) Slow explosions of the gunpowder class.
- (4.) Quick or detonating explosives.
- (5.) Influence of shape of the vessel.

Whether equilibrium will obtain among the products will depend in a general way upon the relation between the rate of decomposition and the linear velocity of the molecules, or we can say upon the relation between the time it takes to evolve all the molecules and the time it takes the flying molecules to cross and recross the confining space. At high densities we assume that the instant of maximum tension coincides with the instant of complete evolution of the molecules. Equilibrium in the sense we give it is a statistical one. It is not meant that all the molecules even of the same kind have the same Kinetic energy, but that the *average* amount of energy due to the Kinetic energy of all the molecules in a given small unit of volume in every part of the space is equal.

The Kinetic theory of gases enables us to calculate the average velocity of the molecules of the different kinds if we know the temperature. To apply this theory is equivalent to admitting that a statistical equilibrium of energies obtains

which is the point at issue, but we can still reason with Berthelot that the energy corresponding to these average velocities is a mean when the whole body of gas is considered, although a statistical equilibrium does not hold for small units of volume.

Velocities of Molecules.—We give a short table of the mean rectilinear velocities of certain molecules (generally present in explosive gases) at 0° C., and 760mm., calculated from the

$\frac{3 \cdot p \cdot g}{D}$

relation $V^2 = \frac{3 \cdot p \cdot g}{D}$ in which V is called the velocity of mean

square, p is the pressure (2116.3 pounds) on the square foot. D is the weight of a cubic foot of the gas, and g is the force of gravity taken at 32.195.

Mean Velocities of Molecules at 0° C.

Symbol for Molecule.	Mass.	Relative Kinetic energy of mole- cule—		
		Velocity in feet per second.	($\frac{1}{2}mv^2$)	(6046^2) ²
Hydrogen	H ₂	2	6046	2 ————— 2
Nitrogen	N ₂	28	1616	28 ————— 2
Oxygen	O ₂	32	1512	32 ————— 2
Carbonic Oxide . .	CO	28	1616	28 ————— 2
Water	H ₂ O	18	2016	18 ————— 2
Carbon Dioxide . .	CO ₂	44	1289	44 ————— 2

All these molecules have the same Kinetic energies, the values in the last column being equal.

This table is calculated for an absolute temperature of 273° . If we assume for the sake of argument, and convenience in calculation, an absolute explosion temperature of 3344° —which is a fair average for different explosives—high for gunpowder, but probably low for some high explosives, we have

3344°

will have $\frac{3344}{273} = 12.25$.

273°

The temperatures being proportional to V^2 , to get the velocities for the explosive temperature the figures in the table above must be multiplied by 3.5, the square root of 12.25.

Mean velocities of molecules at 3344° absolute temperature.

Hydrogen H ₂	21,161 feet
Nitrogen N ₂	5,656 feet
Oxygen O ₂	5,292 feet
Carbonic oxide CO	5,656 feet
Water H ₂ O	7,058 feet
Carbon dioxide CO ₂	4,512 feet

(1) *High Density of Charge*.—Attaching no more importance to these figures than they are worth, it is still easy to see that with a slow rate of combustion in a small confining space, such as given in the eprouvettes used for testing explosives for absolute pressures or at high densities, a uniform distribution of energy will be maintained during the evolution of the gases, whereas with explosives which explode by detonation, great inequalities may obtain during the same period in the different parts of the space for lack of time to get a uniform distribution of the molecular energy.

(a) Gunpowder Class.—To illustrate this case, suppose a charge of gunpowder to be fired at high density in a cylindrical space 2in. in diameter and 2in. in length. Let the total combustion occupy $\frac{1}{100}$ of a second. We find that the slowest of the molecules could have travelled an average of 45 feet in that time, and have crossed the vessel 270 times, while the swiftest, the hydrogen molecule, could have made the journey 1266 times.

There is no violence in the supposition that the energy is uniformly distributed from the beginning of the decomposition,

and remains so till the last molecule is evolved. This supposition is favoured also by the fact that the velocities given above are the means of both higher and lower velocities—an inequality which would hasten the distribution.

(b) Detonating Explosives.—In this case the time occupied by the evolution of the gases will depend upon the velocity of detonation or the velocity of the detonating wave in the medium. In preceding chapters we have given some data on this subject. The velocity of detonation varies in different high explosives. We can take the average rate as 15,000ft. a second without great error. The explosion of the charge in the little 2in. vessel will take something less than $\frac{1}{900}$ of a second for completion. The velocity of the explosive wave is greater than the average velocities of the molecules in the table above. This is equivalent to saying that before the first gaseous molecules evolved can move across the greatest dimension of the vessel, the decomposition is complete. Equilibrium or uniform distribution of the energy which, according to the Kinetic theory, must result from innumerable collisions and interchanges of energy among the molecules, is evidently out of the question.

In case (a) supposing a crushing piston to be used in conjunction with the eprouvette, the action is a "pressure" from the start, and this is in equilibrio with the copper resistance throughout the crushing.

In case (b) the action is a dynamic effect—a blow, and the record on the copper is one of work.

(2) *Low Densities of Charge.*—This is the case where the explosive occupies but a small portion of the available space, and the gases have plenty of room for expansion. We can apply the table of molecular velocities at the explosion temperature as before, and for convenience suppose the charge to be the same as in the small vessel. Then the time of combustion of the gunpowder, and the time for complete detonation of the high explosive, may be taken the same as in the preceding discussion.

In case (a)—gunpowder—the molecules will fly from the seat of the charge towards the walls of the vessel in rapid suc-

cession as they are evolved. If the location of the charge, and the shape of the vessel favour it, there may result a movement of the products more or less as a whole in a certain direction, resulting in an abnormal pressure in the direction of this movement. The action still remains a pressure, but precautions are necessary to make the crusher or other gauge give a record which shall represent a mean. If we can trust the results of General Rodman's experiments with large shells, even a symmetrical disposition of the charge will not ensure. This means pressure on the walls if the path to be covered by the molecules is unduly long.

In case (b)—detonating explosives—the same remarks will apply with, however, some strong qualifications. The average velocities of the molecules will be somewhat greater than in the case of gunpowder, on account of a higher temperature, but the marked difference will be that the time of complete evolution of the gases will be about $\frac{1}{900}$ of the time for gunpowder, so that the molecules will start upon their journeys almost simultaneously. As the molecules get approximately the same start, they will act less as pilots for each other, and the phenomenon of a “line or lines of least resistance,” which is a characteristic feature of the working of gunpowder when the conditions are favourable, will be less marked, while the inequality of velocities in the different kinds of molecules will tend to distribute the energy. The conclusion is that if the density of charge is very low, there will be a strong tendency towards an equalisation of the energy throughout the space before the maximum action on the walls can be exerted. *The instant of maximum action upon a gauge will not coincide with the instant of complete detonation, but will come at a very short period later, when the gases have had time to fill the space and interchange energies*, so that there will always be some loss of energy through heat communicated to the walls of the vessel. On the other hand, this will be partly, or, perhaps, more than compensated for by a ballistic effect of the gases upon the gauge. Both effects are probably small. The first can be allowed for, as shown by Bichel (see last chapter). Though the reasoning is less obvious than in the case of gunpowder, the

ballistic effect will probably depend to some degree upon the shape of the vessel, but this has not been investigated by practical experiment so far as we know.

Bichel's Results.—In the last chapter we gave the latest attempt to measure experimentally the pressure of explosives of both classes under low densities of charge. These experiments were made by Herr C. E. Bichel, using a spring dynamometer. The range of densities covered was from $\frac{1}{150}$ to $\frac{1}{25}$. Herr Bichel does not seem to have troubled himself with some of the difficulties we have raised, especially the possible ballistic effect of the gases. The account given in his little book, "Testing Explosives," may, however, be too brief to give his preliminary studies, and the precautions taken to avoid or to get compensation for this effect. It is possible that some of the variation in the pressure which followed a change in the surface area of the exploding chamber, and which he ascribes to cooling, may have been due simply to the change in the shape of the vessel, which gave a greater, or less value, to this ballistic effect. However this may be, his general arrangement seems well calculated to give reliable values for the pressure. The difficulties we refer to would probably be greater in the case of gunpowder than in detonating explosives, and since we have already shown that his absolute pressure for gunpowder agrees fairly well with Nobel and Abel's figures, when the presence of the solid products is allowed for, we can accept his values for the pressures of high explosives with some confidence.

We will now notice some theories of explosion proposed by their authors to explain certain phenomena which are not well covered by the orthodox view.

Emmens' Ballistic Theory.—A brilliant but unsound paper by S. A. Emmens (the inventor of an explosive called "Emmensite") was published in the Proc. U.S. Naval Inst., No. 59, 1891, entitled, "Explosives and Ordnance Material," in which the author proposes a Ballistic Theory of Explosives. He gives original and striking views of the phenomena attending explosion, and combats with great vigour the doctrine of the "equilibrists," who assume that during explosion the gases are in equilibrium, and act equally in all directions; nevertheless

we will find that he is himself an "equilibrist" of the rankest kind.

The following is a brief summary of his theory:—The energy of an explosive is made up of two factors—a mass factor (the mass of the gaseous products) and a velocity factor. He considers the energy proportional to the pressure developed under certain standard conditions, and obtains the relative velocity factor by dividing this pressure by the mass. He attaches great importance to the relation between the mass and velocity factors.

"The character of the blow as regards the effect produced upon the body struck must be different in the cases of two projectiles, one of which (say a molecule of carbonic anhydride) weighs 22 times as much as the other (say, a molecule of hydrogen), even though the energies of the two blows be equal."

This point is further elucidated by the ingenious conception of a product-molecule for each explosive. The number of molecules in the gases evolved by any explosive being proportional to the reduced or standard volume, if we divide the pressure representing the total energy by the reduced volume, we get the relative energy of the product-molecule for that explosive.

The author illustrates this by a calculation for nitro-glycerin and mercury fulminate, and gives the following comparison and comments:—

	Total energy of molecule.	Mass factor	Velocity factor.
Nitro-glycerin	42.08	1.4035	29.98
Mercury fulminate ..	93.29	3.177	29.37

From this it is at once evident that the fulminate molecule will strike a blow more than twice as severe as that inflicted by a nitro-glycerin molecule, and therefore its penetrative power must be really greater. It is true that weight for weight exploding nitro-glycerin is more powerful than mercury fulminate in the proportion of 29,981.92 : 29, 366."

The comparison contained in the last sentence, which makes the energies of nitro-glycerin and mercury fulminate virtual equivalents is enough in itself to condemn the author's theory.

The ground work of this is contained in the following sentence:—

"The total energies of explosive gases are represented by the total pressures they are capable of producing in the spaces occupied by the explosives."

That is, the total energy of an explosive is measured by what we have called its absolute pressure. But this is very far from being true. The statement confuses the intensity factor of an energy with the energy itself. Moreover, it only considers that part of the energy which we have called the Kinetic, and this under a condition which does not give its real value. It is only when the volume is unity that the pressure becomes numerically related to the Kinetic energy. This singular error on the part of the author has betrayed him into a number of curious conclusions. According to these, dynamite has a greater ballistic energy than nitro-glycerin or even blasting gelatin, and mercury fulminate more than twice as much as any of the others.

The radical defect of the Emmens' theory is that it assumes the total energy of an explosive to consist in the Kinetic energy of the gases, or, more accurately, in the intensity factor of this energy, under a special condition. It takes no account of the store of internal energy which is drawn upon during the expansion of the gases and contributes largely to the work.

In regard to the character of the blow struck by heavy product-molecules moving relatively slowly, or light product-molecules moving swiftly, we must not attach too much importance to this, because the author himself shows that we must reckon with each striking molecule individually, which does much to cripple the fanciful, but otherwise useful, conception of the product-molecule.

The title of the Emmens' theory is suggestive, and the fundamental idea is well founded. In much that the author has to say regarding the fallacies of equilibrium, he has our

sympathy. Many of his most striking statements carry conviction with them. In contending that the gases of detonating explosives are not in a state of equilibrium he is certainly correct, at least, for their most violent manifestations; but in developing the ballistic conception he falls into the old net, which Sarran, Berthelot, Nobel and Abel and others, including the least of them, myself, have followed. He deduces his ballistic elements from the pressure, and how is this pressure obtained? It is deduced from the laws of gases, and these are only applicable under the condition that the energy is uniformly distributed, so that at bottom he is as rank an "equilibrist" as the rest of us.

While this inconsistency condemns the paper as a theoretical study, it is nevertheless a valuable contribution to the literature of explosives. The author's views are bold and original, and if he does not succeed in developing a sound theory, he at least shows the inadequacy of the one usually accepted.

Sarran's Theory.—For a very artistic mathematical treatment of explosives we are indebted to the French savant, M. Emile Sarran, *Ingenieur des Poudres et Salt petres*. His papers, originally published in the "Comptes Rendus," 1874-1878, have been translated by Lieutenants Meigs and Ingwersoll, U.S.N., and form the subject matter of Proc. U.S. Naval Inst., No. 28, 1884. In Part 1, "Theoretical Researches on the Effects of Gunpowder and other explosives," he develops a very complete and harmonious theory, based upon the laws of gases, and the principles of thermodynamics. It is well to note that he avails himself of the Clausius hypothesis in regard to the constancy of the specific heats. It is not our purpose to discuss in detail this remarkable treatise, which is still in many respects the standard. To do so would be to condense into the concise language and unified mathematics of a great master much of what we have already said in our own diffuse way. It is in this treatise that we find the first conception of the "force" as a characteristic of the explosive. It is defined as the pressure developed by the unit weight of the substance detonating in unit volume. As we have already seen, the

capacity factor of the Kinetic energy, being units, this gives it a constant numerical relation to this energy.

We only propose to review the paper in regard to matters which we think wrong. In his treatment of dissociation Sarran is completely at sea.

On page 23 of the translation we have mentioned, we find the following:—

"The force of an explosive substance, when entirely dissociated, is proportional to its heat of combustion."

This might be considered simply a blunder, if the context did not show the contrary. The error seems to arise from a misconception of Berthelot's "law of calorific equivalence," thus given by Sarran: "Having given a system of simple or compound bodies in a determined state; if this system undergoes any physical changes, bringing it to a second state, the quantity of heat absorbed or given out depends solely upon the initial and final states of the system. It is the same whatever may be the nature or sequence of the intermediate states."

He calls those reactions which have the same initial and final states "calorically equivalent," or simply "equivalent" reactions. Pursuing the misinterpretation, he goes on to say (page 24) :—

"The force developed by the same explosive substance in varying equivalent reactions or combustions is proportional to the specific volume of the products formed at the instant of maximum tension. By the different values of this element variable with the state of dissociation of the products, may be explained the considerable variation of the "force" even though chemical analysis of the final products and calorimetric determinations remain the same. The italics in the last paragraph are mine.

At the time this was written the subject of dissociation was still more or less obscure, and the connection between dissociation and heat of formation had not been clearly recognised.

The theory is better developed now. We know that at the instant of maximum tension the force depends upon the active heat as well as the specific volume of the products. The active

heat will be determined by the state of combination of the products at this instant, and not by their final state.

This singular error of taking credit for the increase of specific volume due to dissociation, without making a deduction for the heat rendered latent by it, runs through the whole discussion.

He proceeds to calculate the force for several explosives—a lower limit being obtained by using the value of V_0 corresponding to the state of the products gasified, but not dissociated, and an upper limit by using the volume corresponding to total dissociation—by which term is meant here the reduction of the products to the state of diatomic gases.

He next deduces formulas for the force (approximate, but very simple), based on the weight of the permanent gases, and the value of $(n-1)$, n being the ratio of the specific heats—applicable to the two cases—(a) when the permanent gases are simply gasified, and (b) when they are dissociated.

Comparing nitro-glycerin and guncotton with gunpowder, we have the force according to formula (a), that of gunpowder being taken as unity.

Nitro-glycerin	...	4.55
Guncotton	...	3.06

These ratios are shown to agree fairly well with the experiments of Sarran and Roux, in which explosions of the second order were produced. For example, the relative force of guncotton is about equal to that found by the French Commission on Guncotton, viz., 3.20, obtained by comparing the charges first necessary to burst a shell. A similar agreement was found for the nitro-glycerin of dynamite fired with a gunpowder fuse.

Applying the other formula (b), which supposes the products to be reduced to the diatomic conditions, we have—

Nitro-glycerin	...	5.68
Guncotton	...	3.58

This value for the force of nitro-glycerin is shown to agree roughly with a certain experiment of M. Roux, in which liquid nitro-glycerin was exploded in a shell by a charge of gunpowder.

We now quote as follows:—

“Explosives of the first order. But however great the power of dissociated nitro-glycerin may be, it still fails to account for the effects observed when this substance is fired by violent percussion, or by a charge of fulminate of mercury. It results in fact from our experiments with the effect of nitro-glycerin is then at least nine times that of powder.”

Sarran is driven to explain this nine-fold force of nitro-glycerin by assuming that the molecules reduced to the diatomic state by dissociation are still further dissociated into their constituent atoms. He reaches this result by calculating a value for n which will satisfy this condition for the “force,” and finds n sensibly equal to $1 \frac{2}{3}$, the theoretical value deduced by Clausius and others for monatomic gases.*

He modestly says: “We must then either give up the attempt to explain the phenomena by Mariatte’s and Gay-Lussac’s laws, of which formula (49) is a rigid deduction, or suppose that n , the ratio of the two specific heats acquired at the instant of maximum tension, a greater value than 1.40.” (1.40 is his value of the ratio for diatomic gases.)

The same discrepancy which Sarran found between theory and practice can be observed to-day, but we have a simpler explanation for it. I, for one, do not doubt the nine-fold effect of detonating nitro-glycerin as compared with gunpowder in the bursting of a shell, or at least an effect which can not be explained by the relation between the theoretical pressures of the two explosives, but it is only necessary to suppose that in the initial evolution of the gases of a detonating explosive, there may be a great inequality of action in different directions—as assumed in the last chapter—to get an adequate explanation of this and similar anomalies.

*This shows that I am not the first one to conceive the possibility of the elementary diatomic molecules being dissociated. However, I have supposed this dissociation subject to the usual law of increase of volume, but with loss of heat. I have now contemplated *total* dissociation of any class of molecules—even the triatomic.

This supposition need not be taken as disproving the laws of gases on the Kinetic theory, if we keep in mind that these laws require certain conditions for their fulfilment.

What is this "pressure" or effect which Sarran tried to estimate both experimentally and theoretically, while reconciling the two measures. It is the momentum imparted by the molecules of the gases to the unit of area of the confining vessel in a given small period of time. If we consider the molecules individually, this is a dynamic effect. Considering them in their countless numbers, when it is regulated by certain ideal conditions, it is a pressure. For instance, the laws of gases presuppose that this momentum is equal not only for all parts of the confining surface, but is equal throughout the gas; that is, that the energy of the gas is uniformly distributed in all its parts. If this is not so, the laws of gases fail.

These laws are really consequences of a statistical study of the molecules. We learn that a gas so conditioned will experience a division of its total energy into two portions, one of which, the Kinetic, produces the momentum referred to, while the other, the internal energy, does not contribute directly to the momentum, though it will contribute to the work if the gases are allowed to expand. We also learn that the ratio of division depends simply upon the constitution of the molecule—molecules of the same number of atoms having the same total and the same Kinetic and internal energies. Monatomic atoms have Kinetic energy only which has the usual value. But this ideal distribution, as well as division of the energy, is the result of a constant redistribution and exchange between the two forms, due to innumerable collisions between the different molecules. Indeed, the Kinetic theory requires us to conceive error in a state of equilibrium, great differences in the energies of individual molecules of the same class, the laws being worked out for average or statistical energies.

The ideal state is therefore a state in which, to the united powers of our observation, the molecules are uniformly distributed throughout the space occupied by the gas, and the energy is not only uniformly distributed, but is normally divided into

the energy of internal movement of the parts of the molecules, and the energy of translation of the molecules as integral bodies.

But there is nothing in the theory requiring us to believe that the molecules just born of explosive action will instantly assume this ideal state. Our natural conceptions are against such an assumption. A certain time, though it may be almost inconceivably short, is required for them to become uniformly distributed, and to attain the normal ideal state of equilibrium by exchange of energies.

Notwithstanding his errors, Sarran's work retains a remarkable interest. His hypothesis that the ratio of the specific heats may attain the value $1 \frac{2}{3}$, which pertains to monatomic gases, or, in other words, that the molecules may be completely dissociated into their constituent atoms, is absolutely untenable. The heat, which is one of the elements of explosive energy, is due to the formation of complex molecules. With monatomic molecules alone there can be no heat and no explosion. Still, this hypothesis has found an echo in another, which, on the face of it, is more plausible. It has been suggested that the abnormal pressures in detonation can be explained if we suppose the molecules at birth to be endowed with Kinetic energies greater than called for by the laws of gases. This idea is carried to its limits by supposing that the whole molecular energy is Kinetic. But there is only one class of molecules in which the whole energy can take this form—viz., the monatomic, and we can ask, as before, the authors of this startling proposition where the heat is to come from.

Bichel's "Percussive Force."—It is difficult to cover the effects of different explosives by any one theory, and we can say that it is impossible to devise formulas based on such a theory which will bring out clearly even their main characteristics. Thus, the orthodox theory makes no essential difference between gunpowder and blasting gelatin. The pressures and other elements of the energy differ greatly in the two cases, and the differences are matters of degree. This is because the theory takes no account of the time of action or the rate of decomposition. According to the theory the energy of an explosive is the same, whether quickly or slowly de-

veloped. Practically there is a marked difference in the nature of the work of an explosive, depending upon the time consumed in the evolution of its gases. This difference may have for one limit a marked manifestation of work—for the other, none.

Thus in the Quinan crusher gauge, gunpowder gives no result, while blasting gelatin will smash the cylindrical lead plug into a flat disc. In the Trauzl lead block 10 grammes of blasting gelatin will make a large chamber—about 650 cubic centimetres in volume, while the same charge of gunpowder will not give a perceptible enlargement of the charging hole. Now, when we compare two quantities, one finite and the other approximating zero, the ratio between them approximates the infinite. It is true that there is a decided difference between the energies of the two explosives, but according to theory the greatest difference we can find in the pressures under the circumstances is that blasting gelatin gives 3 or 4 times that of gunpowder. While energy remains the most important thing in the nature of an explosive, we must conclude that it is not the only important thing. We may determine every element of the energy, and yet know little about the characteristics of the explosive.

Herr Bichel (see "Testing Explosives," page 56) has done a useful and interesting thing in supplementing the idea of energy with the idea of relative rapidity or intensity of action. He calls the latter the "Percussive Force" of the explosive, and has proposed a remarkably simple expression for it. In a preceding chapter I touched casually upon this subject of intensity of action, and used the term "fulminate effect" in describing this element in the nature of explosives. I used this term because mercury fulminate, though it has little energy, shows this characteristic in a pre-eminent degree.

Herr Bichel proposes this formula as a measure of the "Percussive Force"

$$\frac{Mv^2}{2}$$

in which M is the mass of the decomposition-products, and v is the rate of detonation. A footnote says, the "formula de-

pends upon the assumption that the observed rate of detonation is identical with the velocity of the molecular projection." This assumption is, of course, unwarranted, and it is difficult, if not impossible, to defend the formula by any strictly mathematical reasoning. The velocity of the detonating wave is not directly related to the velocities of the generated molecules—the latter velocity being governed by the temperature of explosion, and not by the rate of their evolution. A better way to reason is this—the dynamic effect on the confining walls will depend upon the *number* of molecules set free in a given short period of time, and this number will be determined by the velocity of detonation. Depending upon the shape of the charge, and the position of the detonator the ratio between the number of generated molecules and this velocity will vary between the limits, the cube and the first power of the velocity. This is the best justification I can see for using the velocity square in the formula. However this may be, the formula undoubtedly gives a rough measure of the dynamic effect, or of what the author calls the "Percussive Force" of the explosive. The student will find a very interesting discussion on the subject of this characteristic in "Testing Explosives," also in appended Table IV. he will find some striking diagrams of the "Percussive Force" for different explosives.

CHAPTER X.

Dissociation.

Review of Practical Tests.—Disagreement with Theory.—Dissociation the Explanation.—Objections to the Accepted View.—Author's Dissociation Hypothesis.—Normal Dissociation.—Heat of Formation.—Work of Dissociation.—General Formulas for Dissociation.—Oxy-hydrogen Flame.

Review of Practical Test. — Reviewing briefly the last two chapters, we note some of the inferences to be drawn from the discussions therein as follows:—

1) The pressures of the Slow explosives, such as gunpowder and the like, can be readily determined at high densities of charge with the copper crusher gauge.

(2) Determining the pressures at low densities presents more difficulty, and precautions must be taken to prevent ballistic effect resulting from the movement of masses of the gas. The shape of the vessel has an influence on this effect.

(3) The pressures of Detonating explosives cannot be determined experimentally at high densities of charge. Attempts to translate the copper compressions into true pressures have failed—first, because the record is one of work; secondly because, under these conditions, the energy is not uniformly distributed, at the instant of maximum tension, and the action is unequal in different directions. The crushing is a dynamic effect made up largely of what Herr Bichel calls the "Percussive Force" of the explosive, which bears no direct relation to the energy or the theoretical pressure.

(4) At low densities of charge the conditions are essentially changed, the gases have more time to distribute the energy, and it seems to be possible to measure with fair accuracy the true pressure of high explosives. Bichel has used a

spring dynamometer with apparent success through a range of
 $\frac{1}{150}$ to $\frac{1}{25}$.

densities from — to —. By applying the law of Boyle, we

can calculate from the observed pressures the pressures which should obtain in accordance with this law at high and even absolute densities. This is as near as we can come to determining the absolute pressures of detonating explosives by experiment.

Disagreement With Theory.—Now a curious anomaly appears in the practical tests. While the experiments on detonating explosives at high densities, when interpreted reasonably, generally give results that are too high, the absolute pressures obtained indirectly from tests at low densities are much too low, if we take the theoretical calculation of the potential energy as a criterion. The results obtained directly at high densities have, however, little bearing, as they cannot be considered pressures. The interesting fact remains that the most reliable practical determinations of the pressures of high explosives are about 50 per cent. of that calculated by the simple theory. According to this theory, the specific heat of the gases are constant with rise of temperature, and bear a constant relation to the complexity of the molecules. If we divide the heat of the reaction by the specific heat of the products, or get the theoretical rise of temperature, dividing this by 273, we get the increase of pressure in atmospheres. The pressure is therefore strictly dependent on the temperature. The experimental determinations of the temperature are not authentic. We have no scale of measurement for high temperatures that can be relied upon. Still there can be no doubt that the theoretical temperatures obtained from the heat by dividing the latter by the normal specific heat of this products are, in most cases, at least double those attained in practice. Moreover this is confirmed by the pressure* which, under certain conditions,

*We have already given Bichel's experimental absolute pressure in atmospheres for blasting gelatin as 16,658. (See end of chapter VIII.) We can compare this with the theoretical absolute pressure of nitro-

can be measured with fair accuracy in the case of explosives and with great accuracy in that of detonating gases which involve the same principles.

Dissociation the Explanation.—Now we can explain the discrepancy in either of two simple ways. We can suppose the

glycerine (given in chapter IV., table IV., as 63,941,000 pounds on the square foot, or 30,213 atms.), since nitro-glycerine and blasting gelatin are approximately equivalent in both density and energy, but the comparison would not be quite fair. In my calculations for table IV. I took the heat of decomposition of nitro-glycerine lower than the value found by the more recent investigators. I accordingly made a special calculation for Bichel's blasting gelatin from the data given in table III., appendix to "Testing Explosives," the data being as follows:—Composition of blasting gelatin 93% N.G., 7% G.C.—density 1.63—heat, 1550 units. Analysis of products, 61.2 % CO₂, 0.4 % O₂, 18.1 % N₂, 20.3 % H₂O. From which we can write the products as follows:—

	100 units of blasting gelatin give	Reduced Vols. (or No. atoms) for calculating spec. heat.		
		Vols.		spec. heat.
		1.3909 Co ₂	2.7818	4.1727
		.0125 O ₂	.0250	.0250
		.6464 N ₂	1.2928	1.2928
		1.1311 H ₂ O	2.2622	3.3933
			6.3618	8.8838

100 British Criths = .5592 pounds, give 6.3618 cubic feet.

1 pound gives 11.38 cubic feet = V spec. volume.

Spec. heat of the products = 8.8838 × 2.422 = 21.51656.

1550

$$\frac{1550}{21.51656} = 7204^\circ = t \text{ --- rise in temperature. } 7204^\circ + 273^\circ =$$

7477° = T — absolute temp.

7477°

$$\frac{7477}{273^\circ} = 27.39 = P \text{ in atms, at spec. vol. (density of charge =}$$

$$\frac{1}{62.425 \times 11.38} = \frac{1}{710.396} \left. \right\}$$

P at unit density = 710.396 × 27.39 = 19,457.75 atms.

P at absolute density of blasting gelatin (1.63) = 19,457.75 × 1.63 = 31,716 atms.

We see that the absolute pressure from Bichel's experiment (16,658 atms.) is 52.5 % of the theoretical relation approximating this will be found for a great many explosives.

specific heat to increase with the temperature, or we can suppose the heat lessened at the instant of maximum tension by a partial dissociation of the products. The heat of the reaction as obtained experimentally in calorimeters depends upon the final state of combination of the products, but this state of combination does not necessarily obtain at the instant of maximum development of energy. The later French authorities seem to have definitely accepted the doctrine of the increase of specific heats. Mallard and Le Chatelier have proposed for the increased specific heats empirical formulas of the form $K\sqrt{ = } \frac{Q}{a + bt}$

a + bt whence $t = \frac{Q}{a + bt^2}$, in which Q is the heat of the reaction, $K\sqrt{ = }$ the increased specific heat, a the normal specific heat, b is a constant and t the temperature attained.

Bichel, using Mallard and Le Chatelier's values for the specific heats, calculates the temperature of exploding blasting gelatine as 3216 deg. C. Taking the data supplied by Bichel, the *theoretical potential* temperature is 7204 deg. C.

While the French formulas for the increase of the specific heats may serve a useful purpose in getting an approximate value for the temperature, they are empirical and not of great value, being based upon practical attempts to measure the temperature, which we have shown to be rough approximations. Menditeaff shows, for instance, that the estimates of the actual temperature of the oxy-hydrogen flame by different observers vary from 1700 deg. to 2400 deg. C. (See footnote 40 on page 172, *Prin., Chem.*, vol. 1.) He wisely observes "That the methods and apparatus for the determination of high temperatures, although they enable relative changes of temperature to be judged, are of little use for determining their absolute magnitude."

The objection, however, to the French view of the specific heat is that the laws of gases are based upon their constancy. If we give up this principle, there is an end to theory.

Objections to Accepted View.—In its application to explosives, dissociation is a subject which has either been ignored or

been very inadequately treated by investigators. Longridge, after a brief and insufficient discussion, arrives at the hasty conclusion that "dissociation does not practically take place in the combustion of powder in a gun." (See page 19, "Internal Ballistics.")

In their classic researches on gunpowder fired in closed vessels, Nobel and Abel concluded that owing to the great pressure, the dissociation was insignificant. In the French school there has been a pendulum swing of opinion. It is not so many years since the idea of even total dissociation (which is both impossible and absurd) was freely indulged in, as in Sarrau's researches. The latest views of Berthelot are given in "Explosives and Their Power," page 12. After a discussion which is unsatisfactory as to the main points, he reaches the conclusion that "the decomposing influence of temperature can therefore be compensated either wholly or in part by the opposite influence of pressure." So far as one can tell, this is the prevailing view at the present time. It is obviously based on the laws that govern dissociation as determined by applying external heat to dissociable gases.

Being of a reflective turn, I have pondered much over these matters, and have been led to adopt certain views in regard to dissociation accompanying explosive action, which I submit to the consideration of students. In working out the details of my hypothesis and applying them, I have possibly gone astray. That is the usual fate of the pioneer. I think that this view of dissociation in the main will be found acceptable.

Many years ago my studies of explosive energy led me to realise the inadequacy of the accepted view of dissociation, viz., that it is absent or, in great part, suppressed by the pressure. As an instance, in studying carefully the copious record of Nobel and Abel's experiments, I made comparisons of the relative kinetic energies of the gaseous products of the English service powder with those of the mining powder in two ways—(a) by calculating these energies directly from the pressures observed at unit density, (b) by making the usual theoretical

calculations* from the heats determined by the calorimeter and from the volume of the gases. According to (a) the mining powder had a superiority of 36 per cent.—that is the relative kinetic energies of the gaseous products of the two powders were as 100 : 136. According to (b) the superiority was 14 per cent., the energies being as 100 : 114. Here was an honest discrepancy which I tried in vain to account for. To suppose simply that Boyle's law was suspended and that the gases gave abnormal pressures at high densities did not help, because both explosives would be affected by the hypothesis. To suppose the specific heats to increase with the temperature only made this discrepancy greater. No reasonable hypothesis in regard to the specific heats or the expansion of the solid products helped matters. At last it occurred to me that my calculated temperatures in case (b) must be wrong, and that dissociation must be different in the two cases. In this was found a simple explanation. Owing to deficiency in oxygen, the gases of the mining powder were much simpler than those of the service powder—that is the molecules contained a smaller average number of atoms, were therefore subject to less dissociation, and

*These calculations were long and tedious, and are not given, as they involve matter extraneous to the present subject. In these calculations, and in all my studies of gunpowder, I have received much help from Prof. Dibus' "Chemical Theory of Gunpowder" (Phil. Trans. Royal Society, 1882), also reprinted in Proc. U.S. Naval Inst. No. 23. It must be remembered that notwithstanding their elaborate experimental work, Nobel and Abel left the *chemistry* of gunpowder in a hopeless muddle. The products were found so variable and complex that they declared it impossible to express the metamorphosis of gunpowder by chemical equations. Berthelot tried his hand to straighten out matters, and proposed a large number of equations, according to which gunpowder might be decomposed to give the observed products. It remained for Prof. Dibus to unravel the tangled threads, and step by step, each founded upon a demonstration, to build up a harmonious theory. He proved that the combustion of gunpowder occupies two stages—a stage of oxidation and a subsequent stage of partial reduction, and deduced equations for both. He also showed that an equation could be constructed to represent accurately the completed metamorphosis. We can only thus briefly notice this remarkable treatise, but it remains the most wonderful example of acute chemical reasoning in the whole situation of explosives—a beacon light to the earnest student.

the theoretical temperature was more nearly realised than in the case of the service powder. Afterwards, when I had developed my theory and was able to calculate approximately the dissociation for the two powders, I got a relation between the kinetic energies closely agreeing with (a), viz., 100 : 136.

One of the most striking inconsistencies in the accepted view is this. All the authorities agree that in closed vessels, allowing for cooling, which varies with this surface area and is relatively greater for low densities of charge, the temperature is constant for all densities. Thus we quote from Berthelot, page 28, "Explosives and Their Power"—

"1.

Now if bodies susceptible of being completely transformed into gas at the temperatures of the explosion be operated upon, Mariotte's law shows that the pressure developed should be proportional to the density of the charge. The temperature, moreover, would remain the same in all cases."

But the temperature varies with the dissociation. If one is constant, the other is constant also. Then how can the dissociation depend upon the pressure which can be made to vary enormously by varying the density of charge?

It might be answered that Berthelot does not say positively that the temperature is constant for different densities, but makes this constancy depend upon Mariotte's (Boyle's) law. But Bichel has proved that this law holds through the range of

1 1

densities — to — for a variety of explosives, and in the case
 150 25

of gunpowder, that it holds approximately for the gases up to the highest densities.

The accepted view in regard to dissociation is evidently based on the phenomena attending the application of external heat to dissociable gases. It seems to me that the investigators, in applying the same principles without modification to explosive reactions, have been hasty, if not altogether wrong.

When a gaseous system is partly dissociated by applying heat from without (a), the conditions are essentially different from (b) those of a substance undergoing an explosive reaction.

In (a) we have a true case of thermolysis without chemical action.

In (b) the dissociation is the result and accompaniment of an internal action—a chemical union of atoms.

In (a) the gas is already formed and is subjected to heat-created extraneous to the system.

In (b) the elements exist in prior combination, and the gas is formed from them by virtue of a greater development of energy in the new state. The heat applied is that generated in this change of state.

In the first case (a) the heat or temperature is the independent variable—the greater the temperature, ceteris paribus, the greater the dissociation.

In the second case (b) the temperature cannot be the independent variable, since it depends upon the amount of the dissociation—the greater the dissociation the less the temperature. It therefore seems absurd in a particular case to say that the dissociation is governed by the temperature, when we know the latter is governed by the dissociation.

In case (a) the temperature being the independent element, the pressure at constant volume, or the volume at constant pressure, is generally increased by dissociation.

In case (b) the pressure is always diminished by dissociation. It therefore seems absurd to say that the dissociation is diminished by the pressure. If the pressure controls the dissociation, what determines the pressure? The accepted view is a case of reasoning in a circle. The dissociation is acknowledged to control the temperature, and the temperature to control the pressure; if the pressure controls the dissociation, the circle is complete, but we are no wiser than before.

Finally in case (a) the heat applied bears no relation to the stability of the gas. In case (b) the heat is a measure of this stability, being its own heat of formation.

Author's Dissociation Hypothesis.—In my study of dissociation, I have reasoned briefly as follows:—Heat is the decomposing element in nature. Every gas containing more than one atom to the molecule is subject to thermolysis or decomposition by heat.

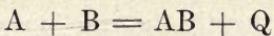
When a gas is heated, a portion of the added energy takes the form of kinetic energy or movement of the molecules as entities. This can have no direct tendency to decompose them. Another portion is converted into internal or interatomic energy, which consists in the motions of the parts of the molecules. We believe that the decomposing influence of the heat lies in this portion of it. We do not know the nature of these atomic motions, but whether we conceive them to be vibratory or rotary, both conceptions are consistent with this belief. Increase of internal heat increases the amplitude of vibration or increases the centrifugal force of rotation, both effects tending to break the bonds uniting the atoms. The idea is also supported by common observation. It is known that the susceptibility of a gas to thermolysis in a general way increases with its complexity or the number of atoms to the molecule. But according to the kinetic theory, the internal energy increases also with the complexity of the molecules. These conceptions serve to emphasise the fact that the gaseous molecules cannot withstand an indefinite increase of its internal energy; consequently the constitution of a gas is limited to a comparatively small number of atoms to the molecule. In the solid or liquid state there is no such limit. Among organic compounds there are molecules supposed to contain a thousand or more atoms, but none of these molecules will bear vaporising without decomposition.

Since a gas producer, by its formation of heat sufficient to wholly dissociate it, if applied as active heats to the gas, it follows that the complete and instantaneous formation of a gas without cooling of the products of the chemical action, is an ideal thing impossible of attainment. I have therefore indulged the conception of a certain percentage of dissociation which is normal to the formation of the gas that is to its initial state of combination before the system has lost any heat. This "normal dissociation" depends upon the ratio between the interatomic energy and the whole energy or upon the molecular constitution. Following certain relations deduced from the kinetic theory, I have been able to propose simple formulas for the normal dissociation of both triatomic and diatomic gases.

What is more difficult, I have tried to modify these formulas so that they can be applied to detonating gaseous mixtures, such as hydrogen and oxygen, hydrogen and chlorine, carbonic oxide and oxygen, etc., in which the pressure can be accurately measured. The pressure calculated from the dissociated system, shown by the modified formulas, gives generally a close agreement with that found experimentally. The difficulty of applying the formulas arises in this way. The conception of normal dissociation is simple, but it is based upon ideal conditions, viz., the formation of a gas from and its partial dissociation into, its constituents without complication, but generally the heat developed causes also a partial dissociation of the constituents as well, and if these are elementary diatomic gases, we do not know their heats of formation, a necessary element in the calculations. Consequently I have been obliged to make certain assumptions in regard to those heats.

In the early part of this chapter I have given reasons for thinking that in an explosive reaction the dissociation is independent of the pressure. I shall now try to show that when a gas is formed from its constituents as the result of chemical action, what we have called its normal dissociation is practically independent of the heat—in this case the heat of formation.

While we do not presume to measure the stability of a gas—that is its resistance to decomposition—in every sense by its heat of formation, for instance, its stability against chemical action—we do measure its stability against heat by this quantity. This is one of the first principles of thermal chemistry, and the orthodox way of writing a thermo-chemical reaction embodies the principle. Thus we write:



That is the gas AB in its formation from its constituents A and B gives out a heat Q, this being the heat of formation. We can reverse the members of the equation and it will still be true.



That is if the heat of formation Q be applied without loss to the gas AB, the gas will be dissociated into its constituents A and B. In other words, the energy which must be overcome in

breaking up a molecule into its constituents is its heat of formation from these constituents. Therefore the stability of a gas against heat is its heat of formation. But we know that the dissociation *ceteris paribus* is also dependent upon the heat, therefore stability and weakness go hand in hand. A great heat of formation tending to a large percentage of dissociation will produce no more dissociation than a small heat of formation, because the resistance to dissociation in the first case will be proportionately larger. Therefore the normal dissociation accompanying the formation of a gas is independent of the heat.

The temperature corresponding to the heat Q is the potential temperature which is now attained—the actual maximum temperature being much lower. In any particular case this actual temperature is governed by the amount of the dissociation. The actual temperature therefore cannot be said to govern this dissociation, since the latter must be regarded as the antecedent.

When an explosive reaction takes place by which a gas is formed from its constituents, the initial state of combination, which is also the state of maximum tension, is one in which only a part of the gas is formed, and only a part of the potential heat is developed. This may be called the active heat. The other portion corresponding to the constituents still disconnected is latent for the time being, to become active as the cooling proceeds and it becomes possible for them to unite. Now we are driven to take this view, because if in the initial state all the constituents united, they would produce a heat sufficient to disunite them all, and there would be no development of heat—consequently the reaction would be impossible—a case of *reductio ad absurdum*. Dissociation may therefore be regarded as a principle of nature. Without it such reactions would be impossible.

Normal Dissociations.—In looking about for some principle to regulate what we have called the normal dissociation of a gas in its initial state of combination, we have been led to believe that it must lie in the nature of the gas itself, with reference to the division of its heat energy into Kinetic and

internal energy, or, to use Hernholtz, wider generalisation into its "free" and "bound" energy. We concluded that the Kinetic energy could have no influence in decomposing the molecules, but that the decomposing influences of the heat must lie in the internal portion, or that which gives motion to the parts of the molecule with reference to its centre of mass. According to the Kinetic theory, the relation between these two energies tends to a constant ratio at all temperatures, and is the same for gases having the same complexity—that is, the same number of atoms to the molecule. Reverting to the initial state of combination of a gas formed by an explosive reaction the simplest view we can take is that the active energy developed in the initial state bears the same relation to the whole or potential energy, that the Kinetic energy of the molecule bears to its whole energy, that is, in normal dissociation the total or potential energy (heat of formation) is divided into active and latent energy in the same proportion as the total energy is divided into the Kinetic and internal energies ascribed to the molecule by the Kinetic theory.

We can arrive at the same conclusion by a slightly different course of reasoning. When the explosive reaction takes place, the system is one of the conflict and equilibrium of certain forces. The energy of union tends to combine all the components of the gas, while the internal energy that would be developed by union tends to dissociate them. We have seen that all the components cannot unite in this initial state, because the development of internal energy would be sufficient to break all the bonds—so that the supposition is absurd. We must suppose a certain number only of the possible molecules to be formed, the remainder continuing in the state of disunited or dissociated components. To determine the percentage of these, we must reason that the decomposing element of the heat, which is the total potential internal energy of the system, is in equilibrio with the energy of union of these dissociated molecules—(more properly the ones that are kept from uniting) or the latent heat of this system—the active energy being that of the united molecules.

We will now find it useful to make a table embodying some of the relations deduced from the Kinetic theory of gases.

TABLE.

Ratios and constants concerned in the Kinetic theory of gases.

Let E = total energy

$$\text{ratio } B = \frac{E}{E_k} \frac{K_p}{K_v} = \text{ratio of specific heats.}$$

E_i = internal energy.

E_k = Kinetic energy.

K_v is proportional to E the total energy. The Kinetic energy E_k is the same for equal volumes of all gases. $K_p - K_v$ is constant for all gases. When K_v for diatomic gases is taken as unity, $K_p - K_v$ for all gases is equal to 0.41. K_v for the unit mass of hydrogen is 2.422 units, which may also be taken as the specific heat of the volume of hydrogen corresponding to the unit mass. K_v for volumes of all diatomic gases equal to this volume of hydrogen will have the same value, and $K_p - K_v$ for all gases is equal to 0.993 heat units = 2.422×0.41 .

Class of Gas	Specific heats for equal volumes.									
	E _k taken as 1			K _p E = ratio	Percentage of E _i & E _k — E		Diatomc K _v = 1		K _v for hydro- gen = 2.422	
	(No. Atoms)	E _i	E _k		E _i	E _k	K _v	K _p	K _v	K _p
Monatomic	0	1	1	1 2-3	0	100	.615	1.025	1.4895	2.4825
Diatomic	.626	1	1.626	1.41	38.5	61.5	1	1.41	2.422	3.415
Triatomic	1.439	1	2.439	1.273	59	41	1.5	1.91	3.633	4.626
Tetratomic	2.252	1	3.252	1.205	69.25	30.75	2	2.41	4.844	5.837
Pentatomic	3.065	1	4.065	1.184	75.4	24.6	2.5	2.91	6.055	7.048

Note.—2.422, the specific heat of hydrogen (that is, the specific heat of unit mass) is also called its atomic heat—the atomic mass being 1. The molecular heat is $2 \times 2.422 = 4.844$. This is the same for all diatomic molecules.

This table shows for the different classes of gases the relations between the energies, internal, Kinetic and whole energy of the molecule.

According to one dissociation hypothesis, these same relations obtain between the dissociated molecules, the united molecules, and the whole (or possible) number of molecules in the

initial state of an explosive reaction between the constituents of a gas.

Let the possible or whole number of molecules of the system be 100, then the percentages in normal dissociation will be as follows:—

	Molecules dissociated.	Molecules formed.
In the formation of a diatomic (2 atom)		
gas	38.5	61.5
triatomic (3 atom)		
gas	59.	41
tetratomic (4 atom)		
gas	69.25	30.75
pentatomic (5 atom)		
gas	75.4	24.6

To illustrate the hypothesis, and show its bearing on the heat relations of the system, we take the case of a triatomic gas, such as H_2O , formed from its diatomic constituents.

Suppose we have 100 molecules of hydrogen and 50 molecules of oxygen capable of forming, with cooling of the products, 100 molecules of H_2O . Let Q represent the heat of formation of one molecule of H_2O . Let the 150 diatomic molecules receive the detonating impulse and react. Then, according to the hypothesis we will have molecules formed, 41 H_2O $\times Q = 41 Q$ active heat developed. Components not united (dissociated), 59 ($\text{H}_2 + \text{O}$) $\times Q = 59 Q$ latent heat

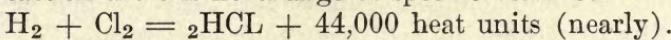
$$\overline{} \quad 100 \quad \times Q = 100Q \text{—potential heat}$$

While normal dissociation gives approximately the initial state of combination of the products of the explosive reaction, it presupposes certain ideal conditions, one of which is that the constituents of the gas themselves do not undergo dissociation. Such an ideal case would be the formation of a diatomic gas from its monatomic constituents—a case not met with in practice. In the case given above for a triatomic gas, if we suppose 41 molecules to unite they will give out great heat, and this may be supposed to dissociate some of the molecules of hydrogen and oxygen, which will tend to lessen the active heat, and this again

will react on the system, and lessen the number of molecules of H_2O dissociated. Another ideal condition is that the heat rendered latent is the true heat of formation of the dissociated molecules. This is only exactly true when either the constituents are confined at constant volume, or there is no change of volume due to dissociation. To apply the principle, therefore to the practical case, it is necessary to deduce special formulas. We will first consider the formation of the gas, and the heat evolved under different conditions.

Heat of Formation.—Thermachemists consider the heat of formation of a gas under two conditions: at a constant volume and under constant pressure. For some gases there is a difference, for others, none. The theoretical heat of formation of a gas is the heat given out by the union of the constituents of formula mass (or* mass of the molecules)—the temperature of the primitive state (that of the constituents) as well as that of the final state being taken as $0^\circ C$. We will consider two cases.

Case (a).—If we take equal volumes of hydrogen and chlorine at this temperature, and cause them to combine, so that the heat is taken up by a large quantity of water kept at, or near, $0^\circ C.$, we find that one molumass (365 units) of the resulting HCl will heat about 22,000 units of water 1 degree. In this reaction there is no change of specific volume:



A given volume of the constituents gives the same volume of hydrochloric acid gas. There is no work done either by or on the reacting gases due to change of volume, and no change in the heat of formation depending upon whether the reaction takes place at constant volume or under constant pressure.

Case (b).—If we consider the formation of gaseous H_2O from hydrogen and oxygen molecules, we have a different case. Three volumes of the constituents contract to two volumes of H_2O in the reaction, so that if the union takes place under atmospheric pressure, work (negative) is done *by* the reacting gases, or positive work is done *on* the gases, equal to the pro-

*A convenient term for this can be invented, viz., *molumass*. Prof. Chas. E. Monroe has proposed the term *molugram*, but this limits the unit of mass to the French system.

duct of the constant atmospheric pressure and the change of volume. This work is converted into heat, and increases the heat observed.

When the constituents and final products are confined at constant volume, that is, the reaction takes place in a closed vessel, there is no actual change of volume, and no work is done, due to the change of specific volume. The heat observed is therefore the true heat of formation. We thus reach the conception of a true or ideal heat of formation which is realised for all gases only, when either there is no change of specific volume in the reaction—case (a) or if there is such a change—case (b), when the constituents and final products are confined to constant volume.

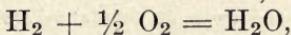
In every case the heat given out at constant volume is the true heat of formation.

There is a general formula used by thermochemists (see "Explosives and Their Power," p. 122), for passing from the heat of formation under constant pressure, to that at constant volume or the reverse, when one or more gases are formed from others by a chemical reaction—the temperature of the constituents and final products being 0° C. The formula may be written as follows:—

$$(A) \quad Q_v = Q_p + 542 (N^1 - N),$$

in which Q_v and Q_p are the respective heats of formation at constant volume and constant pressure, N^1 is the number of molecules in the products, and N the number of molecules in the constituents.

If we apply this formula to the reaction,



we find $N = 1\frac{1}{2}$, $N^1 = 1$ and $N^1 - N = -\frac{1}{2}$.

Accordingly, we have, in this case,

$$Q_v = Q_p - 271.$$

Work of Dissociation.—To estimate the heat rendered latent by dissociation we must take into account the work (if any) due to change of volume.

(a) We consider first the case of a gas which undergoes a certain amount of dissociation with increase of specific volume (the general case) under constant pressure. The heat rendered

latent is equal to the true heat of union of this amount of gas plus the work (taken as heat) done by virtue of the increase of volume. We can express this by the equation

$$L_p = Q + \frac{W}{J}$$

Since the molecule represents a definite volume we can take this equation as applying to the molecule as a unit change of volume — L being the heat rendered latent by, and W the mechanical work of, the dissociation, which produces this change.

(b) If we consider the dissociation of a gas at constant volume, that is, in a closed vessel, we will have simply

$$L_v = Q.$$

If there is no change of volume, then in all cases $L = Q$.

In case (a), dissociation under constant pressure, W^* is equal to $(V_1 - V_0) P_0$, in which $(V_1 - V_0)$ is the change of volume due to dissociation, and P_0 is the constant pressure.

When there is no change in the specific heat—that is, when the specific heat of the molecule is the sum of the specific heats of its components, we can calculate the work of dissociation from the fundamental equation $W = pv = J(K_p - K_v)$, in which v represents the change of volume under constant

*The student may be puzzled over these formulas, $L_p = Q + \frac{W}{J}$

and $L_v = Q$. He may reason that the heat work of dissociation at constant pressure being $(+ \frac{W}{J})$, the work at constant volume should be $(-\frac{W}{J})$,

because the work of dissociation is isothermal (both the constituents and products being 0°C.), therefore according to Boyle's law $(V_1 - V_0) P_0$ is equal to $(P_1 - P_0) Vq$. But this law does not apply to case (b) confinement at constant volume. In this there is no mechanical work done, there being no actual change of volume. Joule has shown that in a perfect gas, elastic changes (in this case a change in the specific volume leading to an increase of pressure) that do not involve work produce no change in the heat of the gas, therefore $\frac{W}{J} = 0$.

pressure, p —or p represents the change of pressure at constant volume v .

To convert the work pv into heat, divide by J ; we then have $h = K_p - K_v$.

To compute the value of h in heat units for change of volume corresponding to one molecule, we take advantage of the fact that $K_p - K_v$ is equal to 0.41 for all molecules when the specific heats are compared with that of a diatomic molecule taken as unity.

The specific heat of a diatomic molecule in heat units, being 4.844 (twice 2.422), the total energy of such a molecule at the standard temperature, 0° C., or 273° absolute, will be $4.844 \times 273 = 1322$ heat units. The work h corresponding to its total volume is therefore (total) $K_p - K_v = 0.41 \times 1322 = 542$ heat units (nearly).

But since all molecules occupy equal volumes under like conditions, this is the difference of the work of dissociation (taken as heat) for a change of volume corresponding to any molecule.

There is a special case, however, to be considered in the dissociation of a diatomic gas into its monatomic constituents, because there is a change of specific heat during the reaction. We arrive at the heat relations as follows, taking hydrogen as an illustration:—

The total specific heats or energies at 0° C. will be for the two classes of molecules.

1 molecule, H_2 diatomic = 1322 units (813 Kinetic—509 internal).

2 molecules, $H + H$ monatomic = 1626 units, all Kinetic.

1 molecule, H monatomic = 813 units, all Kinetic.

Since the monatomic molecules resulting from the dissociation of a diatomic occupy twice the volume of the diatomic, there is a gain of one diatomic volume by dissociation which determines the work W , and makes its heat equivalent 542 units, as before. However, in passing from one state to the other (one diatomic to two monatomic), there is a gain of energy equal to 304 units of heat, therefore the true heat of formation is not the same as the latent heat of dissociation even

at constant volume. If we assume that the true heat of formation of H_2 from $H + H$ is some quantity Q , then Q_v , the heat that would be observed at constant volume will be $Q - 304$; but as we do not know, and cannot compute, the value of Q , let us take Q_v as the heat of formation at constant volume, then Q_p will be $Q_v + 542$, hence $L_v = Q_v$ and $L_p = Q_v + 542$.

The case of a diatomic gas formed from or dissociated into diatomic constituents is simple. There being no change of volume, in all cases we have $L = Q$.

From the foregoing discussion we see that the latent heat of dissociation of a molecule is its heat of formation under the special conditions.

General Formulas for Dissociation.—By applying the principle that the potential internal energy is in equilibrium with the heat rendered latent by dissociation, we reached the conclusion that the dissociation normal to the formation of a triatomic gas from its constituents is 59 per cent. of the possible molecules. By the same course of reasoning the normal dissociation of a diatomic gas is 38.5 per cent. of the possible. We call these percentages the normal percentages. The hypothesis is ideal in supposing that the constituents exist as such in the primitive state, and that the dissociation is confined to the gas itself.

The principle of the equilibrium between the forces mentioned will be taken as our general guide.

There are several cases to be studied.

(1) The case we have already partly considered is the dissociation normal to the formation of a gas from its constituents confined at constant volume. This and case (2) are peculiar, because the term dissociation is, strictly speaking, a misnomer—the so-called dissociated molecules being constituents, which have not been united to form molecules of the gas. We adhere to the term dissociated as applied to these molecules simply for convenience.

Then number N out of a possible 100 will be:

For a triatomic gas, $N^{111} = 59$.

For a diatomic gas, $N^{11} = 38.5$ (formed from diatomic constituents).

For diatomic gas, formed from monatomic constituents, we have $N^{11} = 38.5$ (the heat rendered latent is $38.5 Q_v$).

(2) To calculate the normal dissociation when the gas is formed from its constituents under constant pressure, we apply the general principle that the latent heat is equal to the potential internal energy.

Let N be the number of molecules dissociated out of a possible 100—we have,

For a triatomic gas, $N^{111} (Q + 271) = 59 (Q + 271)$
(change of vol. = $\frac{1}{2}$ diat. mol.), $N^{111} = 59$, $L_p = Q + 271$.

For a diatomic gas formed from diatomic constituents (no change of volume), $N^{11} = 38.5$, $L_p = Q_v$.

For a diatomic gas formed from monatomic constituents, $N^{11} (Q^{1v} + 542) = 38.5 (Q^{1v} + 542)$, change of vol. = 1 diat. mol., $N^{11} = 38.5$, $L_p = Q^{1v} + 542$.

We see in this case the percentage of dissociation remains normal, but more heat is generally rendered latent than in case (1), on account of the work of dissociation, or, what is the same thing on account of the increase in the heat of formation.

(3) If we suppose the gas itself to be confined to constant volume, and to receive a certain amount of heat, not necessarily its heat of formation, we can get a simple expression for the number of molecules dissociated by applying the general principle.

Let N be the whole number of molecules, H the total heat applied, and h the heat applied to each molecule, thus Q being the heat of formation of the molecule, we have,

$$\begin{aligned} \text{For a triatomic gas, } N^{111} Q &= 0.59 Nh \\ N^{111} &= 0.59 Nh \end{aligned} \quad (a)$$

$$\begin{aligned} \text{For a diatomic gas, } N^{11} \frac{Q}{Q^1} &= 0.385 N^1 h^1 \\ (\text{into monatomic}) \quad N^{11} &= 0.385 N^1 h^1 \\ \text{constituents} & \end{aligned} \quad (b)$$

(4) If we suppose the gas to be under constant pressure, and a certain heat applied, we have, by a similar course of reasoning,

(a¹)

$$n^{111} = 0.59 \text{ Nh} \quad (\text{a}^1)$$

$$\begin{aligned} n^{11} &= \frac{Q + 271}{0.385 \text{ Nh}^1} \quad (\text{b}^1) \\ &\hline Q^1 + 542 \end{aligned}$$

If in cases (3) and (4) we suppose the number of molecules n to be 100, and h the heat applied to each to be the latent heat of dissociation under the conditions which is the same as its heat of formation under those conditions, the percentage of dissociation will be the normal.

$$n^{111} = 59 \quad n^{11} = 38.5$$

and we reproduce cases (1) and (2) respectively.

We can apply these principles to the solution of a number of problems in which dissociation plays a part, such as the temperature of the oxy-hydrogen flame, the temperature and pressure of various detonating gaseous mixtures, etc.

Oxy-Hydrogen Flame.—We will try to determine approximately the temperature of this flame burning under constant pressure. The true heat of formation of gaseous H_2O is that at constant volume, $Q = 57,632$. The heat of formation under constant pressure is $Q + 271 = 57,903$ (this at 0° C . obtained from Thomson's data).

We will first compute the potential temperatures by supposing the hydrogen and oxygen to unite in the proportion of two volumes of the first to one volume of the second, and to form the possible number of H_2O molecules. The rise in temperature would be the heat of formation $Q_p = 57,903$ heat units divided by K_p , the specific heat of H_2O at constant pressure. — $\frac{K_p}{K_v}$

being equal to 1.2733, and the number of atoms in H_2O being 3, we have

$$K_p = 2.422 \times 3 \times 1.2733 = 9.252.$$

$$\qquad\qquad\qquad \frac{57,903}{9.252}$$

$$\text{The theoretical temperature} = \frac{\text{——}}{9.252} = 6258^\circ \text{ C.}$$

This is the potential or theoretical temperature which would be reached in the absence of dissociation.

Dissociation of Triatomic Molecules.—According to our hypothesis for normal dissociation, only 41 per cent. of the triatomic molecules can unite in the initial stage of the reaction, leaving 59 per cent. dissociated.

The heat realised for every possible 100 molecules is therefore $41 \times 57,903 = 2,374,023$ heat units.

The specific heat for 100 molecules of the dissociated system will be

$$\begin{array}{rcl} 41 \text{ } \text{H}_2\text{O} & = & 41 \times 2.422 \times 3 \times 1.2733 = 379.33 \\ 59 \text{ } \text{H}_2 & = & 59 \times 2.422 \times 3 \times 1.41 = 604.46 \\ 59 \text{ } \frac{1}{2}\text{O}_2 & & \hline \end{array}$$

$$983.79$$

$$\text{Temperature} = \frac{2,374,023}{983.79} = 2413^\circ \text{ C}$$

But this result needs a small correction. The heat is not applied to molecules of H_2O throughout the range of temperature. The component hydrogen and oxygen must first be raised to the combining point, say, 600° C . This work is done by the flame itself, when it is once established, and is a tax upon its heat. If we estimate the rise in temperature from the point 600° , the value for the total specific heat given above will be correct.

The specific heat of the component gases will be:
 $100 \times 2.422 \times 3 \times 1.41 = 1024.5$.

The heat expended in raising their temperature to 600° C. will be:

$$600 \times 1024.5 = 614,700 \text{ units, and we have}$$

$$2,374,023 - 614,700 = 1,759,323.$$

$$1,759,323$$

$$\frac{}{983.79} = 1788^\circ \text{ rise in temperature from } 600^\circ \text{ C.}$$

$$1788^\circ + 600^\circ = 2388^\circ \text{ temperature attained.}$$

This result is only approximately correct, since it ignores the possible dissociation of the constituent molecules of hydrogen and oxygen.

Dissociation of Triatomic and Diatomic Molecules.—Our general formulas for the dissociation percentages being as follows:

$$\text{Triatomic, } n^{111} = 0.59 \text{ Nh}$$

$$\overline{Q}$$

$$\text{Diatomc, } n^{11} = 0.385 \text{ N}^1 h^1$$

$$\overline{Q^1}$$

We have, when suitable values for Nh and N¹h¹ are substituted, and the equations solved (the details of the calculation will be given later in the treatment of the detonating mixtures of hydrogen and oxygen),

$$n^{111} = 53.35, \text{ leaving } m^{111} = 46.65$$

$$\overline{Q}$$

$$n^{11} = 9.58 - \frac{}{Q^1}$$

Q under the conditions is Q_p = 57,903 units. Q¹, for reasons given later, is assumed Q_v + 542, or 38,421 + 542 = 38,963,

$$\overline{Q}$$

and $\frac{}{Q^1} = 1.4604$, whence n¹¹ = 13.99.

For every possible 100 molecules of H_2O (consisting of 300 atoms), the dissociated system will be as follows:

Triatomic molecules, $m^{111} = 46.65 \times 3$	$= 139.95$ atoms
Diatomie molecules, $m^{11} = 66.03 \times 2$	$= 132.06$ atoms
Monatomic molecules, $m^1 = 27.99$	$= 27.99$ atoms

Total molecules	140.67
-------------------------	--------

The heat rendered latent will be:

$$n^{111} Q = 53.35 Q$$

$$n^{11} Q^1 = 9.58 Q$$

$$\underline{\hspace{2cm}} \\ 62.93 Q$$

The active heat, $100 Q - 52.93 Q = 37.07 \times 57,903 = 2,146,464$ units.

The specific heat of the dissociated system is computed as follows:

molecules		
$m^{111} = 46.65 \times 3$	$139.95 \times 2.422 \times 1.2733 = 431.61$	
$m^{11} = 66.03 \times 2$	$132.06 \times 2.422 \times 1.41 = 450.99$	
$m^1 = 27.99 \times 1.23$	$34.43 \times 2.422 \times 1\frac{1}{3} = 138.98$	
<hr/>	<hr/>	
306.44		1021.58 = Kp

(See table for explanation of this calculation.)

The heat expended in raising the temperature of the compounds to 600° is 614,700.

$$2,146,464 - 614,700 = 1,531,764$$

$$\frac{1,531,764}{1021.58} = 1499^\circ$$

$1499^\circ + 600^\circ = 2099^\circ$ C. temperature attained by the flame.

We have seen that the estimates of practical observers vary from 1700° C. to 2400° C., so that this falls between

the extremes. Mendeleef considers the mean of the most trustworthy determinations to be about 2000° C. (see *Prin. Chem.*, vol. 1, page 172). As the observed temperature is bound to be a little less than the ideal, for various reasons, such as, imperfection in the preparations of the hydrogen and oxygen, or in their mixture in the burner, loss by contact of the flame with the atmosphere, etc., the result given above, 2099° C., is probably very near the true temperature under ideal conditions.

CHAPTER XI.

Detonation of Gaseous Mixtures.

Detonating Gaseous Mixtures.—Views of Berthelot.—Formulas for Dissociation in a Mixture of Gases.—Detonation of Hydrogen and Oxygen.—Of Hydrogen, Oxygen and Nitrogen.—Hydrogen and Chlorine.—Carbonic Oxide and Oxygen.—Table of Detonating Gaseous Mixtures.

Detonating Gaseous Mixtures.—The gaseous state is the simplest form of matter, and the fundamental laws of explosion can be more readily detected when both elements—the exploding material and its products—are in the gaseous form, than when the metamorphosis involves a change of state. The subject, therefore, forms an important chapter in the history of explosives—a chapter contributed chiefly by Berthelot and his co-workers.

The detonation of a mixture of gases is a familiar experiment to chemical students. If, for instance, we take certain proportions of two diatomic gases confined at atmospheric pressure, which are exactly capable of forming another gas by an explosive reaction, we have one of the cases contemplated in the recent discussion of dissociation. If we suppose that all of the diatomic constituents take part in the reaction, and are transformed into the new gas (that is, there is no dissociation), the calculation of the rise in temperature, and the increase of pressure (we call these the potential or theoretical elements of the energy) is very simple.

The experimental determination of the increase of pressure (which is not excessive) is also quite practicable, so that we have something positive and definite with which to check

the theory. For measuring the pressure various appliances have been used, such as valves loaded with springs or weights, and the registering piston-gauge used by Berthelot and Vicille.

Now when such mixtures as hydrogen and oxygen, carbonic oxide and oxygen, methane and oxygen, cyanogen and oxygen, hydrogen and chlorine, etc., are detonated at constant volume, *it is found that the observed pressure is less than half the theoretical.*

This may be accounted for in one of three ways:—

(1) We may suppose that the gaseous products do not obey the laws of Boyle and Charles—there being an interaction between the molecules involving internal work and consequent loss of heat.

(2) We may suppose, simply, that the specific heats increase with the temperature. In this case, also, the products cannot obey the laws of gases.

(3) We may suppose that dissociation of the products limits the temperature and maximum pressure, which is the thing measured. This supposition is the only one of the three consistent with the laws of gases.

However, the first supposition should not be entirely disregarded. Many gases are very imperfect at low temperatures, because they are too near their critical points to obey the gaseous laws. Their internal energy is greater, and their Kinetic energy less, than is normal to their molecular constitution. The influence of high temperature is to correct this, but in the process there is a certain amount of heat expended (rendered latent), of which the theory does not take account. This loss is the greater for gases notably imperfect at ordinary temperatures, such as chlorine, which have abnormally large specific heats, an abnormally large proportion of which is internal, or bound, energy. Bringing such a gas to the perfect state pertaining to high temperatures involves a certain amount of

internal work, by which heat is rendered latent.* Nevertheless, the theory, like Avogadro's law, can be depended upon to give results which are closely approximate, and in the case of very imperfect gases a special allowance can be made.

The supposition that the specific heats increase with the temperature (except for small intervals of temperature at or near the critical points) is entirely unwarranted, according to our view. Neither is it supported by what we know experimentally of the behaviour of gases at high temperature.

Views of Berthelot.—This matter is discussed by Berthelot (see page 388, "Explosives and Their Power"). He inclines to the belief that the specific heats increase with the temperature. If we agree to this we must also admit that the products do not obey the laws of gases, since these laws are directly dependent upon the constancy of the specific heats.

Let us look into Berthelot's reasoning, and see what has led him into this apparent antagonism to the only theory upon which the study of explosive energy can be profitably based.

Berthelot does not recognise the distinction between the atom and the molecule in the elementary gases. With this

*The normal specific heats of unit mass of chlorine, Cl_2 , should be
 K_p

$K_p = .0962$, $K_v = .06823$, $\frac{K_p}{K_v} = 1.41$. The observed specific heat K_p tends to become normal as the temperature rises. The average up to 200° C. is

K_p
 0.1241 . Up to 343° it is 0.1155 , $\frac{K_p}{K_v} = 1.32$, therefore $K_v = 0.875$. The

K_p
 $\frac{K_p}{K_v} = 1.32$ makes the internal energy approximate that normal to

K_p
 a triatomic gas, for which $\frac{K_p}{K_v} = 1.273$. The internal energy, instead of being 38.5 per cent. of the total, is 52 per cent. A convenient formula for

$$3 \left(\frac{K_p}{K_v} - 1 \right)$$

the percentage of internal energy is $E_i = 1 - \frac{3 \left(\frac{K_p}{K_v} - 1 \right)}{N}$, in which N

is number of atoms in the molecule.

great chemist, hydrogen is H and oxygen is O, and nothing more. According to this view there is no such thing as the dissociation of an elementary gas. This is implied in his dictum that mercury fulminate gives non-dissociable products. Again, in speaking of the explosion of certain endothermal gases, he says, on page 384, "Let us note that here there can be no question of dissociation, since the products of the explosion are elementary gases."

Holding this view, he studies certain explosive reactions, giving only elementary gases as products, and finds, by experiment, that the actual pressure is far below the theoretical. Since there can be no dissociation, there is but one adequate explanation, an increase during explosion of the specific heat.

However, the conceptions of the paired molecule, H_2 , O_2 , N_2 , etc., is one of the corner stones of modern chemistry. If the elementary gases consist of molecules (usually diatomic), why should they form an exception to a law otherwise general that molecules are subject to dissociation?

This is what Mendelieff says on the subject:—(See page 313, vol. 1, Prin. Chemistry.)

"And if compounds are decomposed by a more or less powerful heat, and if polymeric substances are depolymerised (that is, the weight of the molecule diminished) by rise of temperature, as N_2O_4 passes into NO_2 , or Ozone O_3 into ordinary oxygen O_2 , then we might expect to find the splitting up of the complex molecules of elements into the simplest molecule, containing a single atom only, that is to say, if O_2 may be obtained from O_3 , then the formation of O might also be looked for."

We believe we state the opinion of a large majority of scientists, in saying that all gases, including the elementary (with the exception of the peculiar class known as monatomic) are made up of complex molecules, and are subject to thermolysis, or decomposition, by heat.

In discussing the detonation of gaseous mixtures, Berthelot goes on to say: "It suffices to admit the existence of a certain dissociation in order to reduce the pressure by (to) one-half, or even one-third, of the calculated values. Nevertheless, the

rapidity of propagation of the explosive wave (page 101) seems to indicate that at the moment of its production the explosive system contains all the heat liberated by an integral combination. The propagation of the wave is, however, so rapid that the pressure observed probably corresponds in every kind of apparatus to a system which is already partially cooled, and it is this reduced pressure which seems to correspond to the case of ordinary combustion. We might also explain the results observed by accepting the variation of specific heats, especially if we double the mean specific heat of water vapour or of carbonic acid." The general conclusion seems to be that the reduction of the pressure can be ascribed to either cause, dissociation, or increase of specific heats. Berthelot does not exclude dissociation of the triatomic products, but he appears to favour the other view. His reasoning, however, is rather hard to follow. It is difficult to see any necessary connection between integral combination and the velocity of the detonating wave, or correspondence between rapid propagation of the wave and the cooling of the products.

Berthelot and his co-workers made a great many experiments upon detonating gaseous mixtures, of which the following may be taken as a type.

If a mixture of two volumes of hydrogen and oxygen be taken at atmospheric pressure, and detonated at constant volume (in a closed vessel), the theoretical increase of pressure will be a little less than 20 atmospheres, and the theoretical or potential temperature nearly 8000° C. The specific volume of the resulting H_2O (supposing the reaction complete) is only $\frac{2}{3}$ of that of the constituents (or of the confining volume), so that there is no question of crowding of the molecules. If the laws of gases can hold, they should hold good in this case. The temperature is high and the volume great. Even under the usual view, the conditions are favourable to dissociation.

Formulas for Dissociation in a Mixture of Gases.—When we attempt to apply the formulas for normal dissociation to a practical case, such as the determination of the actual rise of temperature and increase of pressure in a detonating gaseous mixture, we are met by some difficulties. It is true we can obtain

rough approximations by ignoring the dissociation of the diatomic gases. For instance, in the case given above, if we ignore the dissociation of the constituents themselves, we find that 41 per cent. of the constituents will unite, and 59 per cent. will remain separated (we say dissociated for convenience) as regards the triatomic product. The increase of temperature will be 41 per cent., and the increase of pressure about 53 per cent. of the theoretical (this takes into account the greater specific volume of the diatomic gases).

But these figures are only approximations. The 41 completed triatomic molecules (out of a possible 100) will generate great heat by their formation, and this will doubtless dissociate some of the diatomic molecules into their monatomic constituents.

The problem to solve is, what will be the relative percentages of dissociation in the two classes of gases? As we do not know the amount of energy which unites the constituents of the diatomic molecules, we can only hope to get a proximate solution.

Let the original number of diatomic molecules be the equivalent of 100 triatomic, that is, let us take 150 diatomic molecules (100 H_2 and 50 O_2) in the gaseous mixture. For simplicity we will suppose all these diatomic molecules to have the same energy of union or heat of formation Q^1 , and Q to be the heat of formation of the triatomic molecule.

We will suppose that when the reaction takes place the initial state of combination (that of maximum tension) shows dissociation of both triatomic and diatomic molecules.

Let m^{111} = number of integral triatomic molecules in the dissociated system.

m^{11} = number of integral diatomic molecules in the dissociated system.

m^1 = number of monatomic molecules in the dissociated system.

n^{111} = number of triatomic molecules dissociated.

n^{11} = number of diatomic molecules dissociated.

Then we have

$$m^{111} + n^{111} = 100$$

$$m^{111} + \frac{2}{3}m^{11} + \frac{1}{3}m^1 = 100$$

$$\text{whence } n^{111} = \frac{2}{3}m^{11} + \frac{1}{3}m^1$$

The active heat to be considered for the system will be:

$$100 Q - (n^{111} Q + n^{11} Q^1) = m^{111} Q - n^{11} Q^1.$$

The heat rendered latent will be:

$$100 Q - (m^{111} Q - n^{11} Q^1) = n^{111} Q + n^{11} Q^1.$$

The total or potential heat equals the sum of these two:

$$(m^{111} + n^{111}) Q = 100 Q.$$

We must regard the dissociated system as an unstable one, in which constant composition and decomposition are taking place. The condition of equilibrium is that the Kinetic energies of the molecules in the system shall be equal. The relative dissociation of the triatomic and diatomic molecules is determined by the relation between their respective energies of union, and the internal energy pertaining to each.

If we could make the temperature the independent variable, the dissociation would be governed by it, because there is a fixed relation between the total energy which determines the temperature and the internal energy which determines the dissociation. In a mixture of gases these energies could be computed for each gas; moreover, reasoning by analogy from the law of partial pressures in a mixture of saturated vapours, we could safely assume that for a constant temperature the percentage of dissociation in a gas would be the same, whether it were taken by itself or mixed with other gases, provided there were no chemical action between them. This is the ideal condition contemplated in what we have called normal dissociation. When the gas is considered mixed with its own components these formulas need modification.

If we admit that some of the diatomic molecules must be dissociated, it follows that this will diminish the temperature otherwise attainable, and the dissociation of the triatomic molecules will be less than the normal.

The dissociation of the diatomic molecules is not normal, because the heat applied is not the heat of formation. The general formula which we must use for their dissociation is given in the last chapter as (b) under case 3.

$$n^{11} = \frac{0.385 N^1 h^1}{Q^1}$$

In which Q^1 is the heat of formation, N^1 the number of molecules, to each of which the heat h^1 is applied— n^{11} being the number dissociated.

If Q^1 were known we could proceed as follows:

Assuming normal dissociation for the triatomic molecules, that is, 59 molecules, we would have an active heat of 41 Q applied to the system, and could calculate the dissociation of the diatomic molecules that had not formed themselves into triatomic. But this would give a latent heat greater than 59 Q . Allowing for the effect of this in reducing the heat, we could recalculate the dissociation of the triatomic, and then that of the diatomic, and so on, by a series of approximations, till we got the real percentage of each.

Not knowing Q^1 , the diatomic heat of formation, we proceed to determine the dissociation in terms of known and unknown quantities, as follows:

Our general formulas are, for

$$\text{Triatomic dissociation, } n^{111} = \frac{0.59 N h}{Q}$$

$$\text{Diatomc dissociation, } n^{11} = \frac{0.385 N^1 h^1}{Q^1}$$

The first step in applying these formulas is to determine the heat to be considered as applied to each gas.

1. In the case of the triatomic gas we consider $N = 100$ molecules. These are subjected to a heat $= 100 Q - n^{11} Q^1$, therefore

$$h = \frac{100 Q - n^{11} Q^1}{100}, \text{ and } Nh = 100 Q - n^{11} Q^1,$$

and we have

$$n^{111} = 0.59 \frac{(100 Q - n^{11} Q^1)}{Q} \quad (\text{a})$$

2. In the case of the diatomic gas, the number of molecules to be considered is $m_1 = 150 - 1\frac{1}{2}m^{111}$.

The heat $100 Q - n^{111} Q = m^{111} Q$ is applied to m_1 diatomic, and m^{111} triatomic ($= 1.5 m^{111}$ diatomic), but $m_1 + 1.5 m^{111} = 150$.

The heat h^1 applied to each diatomic molecule is therefore $\frac{m^{111} Q}{m_1 m^{111} Q}$, hence $N^1 h^1 = \frac{150}{150}$, and

$$n^{11} = \frac{0.385 m_1 m^{111} Q}{150 Q^1}.$$

This in equation (a) above gives

$$n^{111} = 0.59 (100 - 0.385 m^{111} + 0.00385 m^{2-111}),$$

which, with $n^{111} = 100 - m^{111}$, gives

$$m^{111} = 46.653$$

$$n^{111} = 53.347$$

This value of n^{111} in equation (a) above gives

$$n^{11} = 9.58 \frac{Q}{Q^1}$$

We cannot get the value of n^{11} (the number of diatomic molecules dissociated) without knowing the relation $\frac{Q}{Q^1}$.

However, we can assume a succession of simple values for this ratio, and remembering that $m_1 = m^{11} + n^{11} = 1\frac{1}{2}n^{111} = 80.02$, nearly, we get the following values, in which

m^{111} = number integral triatomic molecules in the dissociated system.

m^{11} = number integral diatomic molecules in the dissociated system.

m^1 = number monatomic molecules in the dissociated system.

n^{111} = number triatomic molecules dissociated.

n^{11} = number diatomic molecules dissociated.

$m^{111} = 46.653.$

$n^{111} = 53.347.$

$m_1 = 80.02.$

Diatomie and Monatomic Molecules in Dissociate System,

assuming different values for $\frac{Q}{Q^1}$.

$$m^{111} = 46.653.$$

	m^{11}	m^1
$\frac{Q}{Q^1} = 1$ ($n^{11} = 9.58$)	70.44 ..	19.16
$\frac{Q}{Q^1} = 1\frac{1}{2}$ ($n^{11} = 14.37$)	65.65 ..	28.74
$\frac{Q}{Q^1} = 2$ ($n^{11} = 19.16$)	60.86 ..	38.32
$\frac{Q}{Q^1} = 2.5$ ($n^{11} = 23.95$)	56.07 ..	47.90
$\frac{Q}{Q^1} = 3$ ($n^{11} = 28.74$)	51.28 ..	57.48

If this reasoning be correct, the percentage of dissociation of the triatomic gas is constant (53.347), and independent of the value of Q^1 , while that of the diatomic gas increases directly with the ratio $\frac{Q}{Q^1}$, so that the heat rendered latent by this latter dissociation is constant and equal to 9.58 Q.

In regard to choice of values for the ratio $\frac{Q}{Q^1}$, I have made

a good many calculations of the pressures in various detonating gaseous mixtures, using different ratios, and have compared the results with those of practical experiment. The value $\frac{Q}{Q^1}$

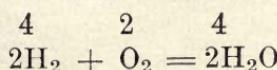
$= 1\frac{1}{2}$ gives the closest agreement, and I have accordingly adopted it in the following computations.

We will now consider several cases of detonating gaseous mixtures. We will first calculate the increase of temperatures and pressures as elements of the potential energy, and then calculate the elements of the energy developed under different hypothesis in regard to the extent of the dissociation, and compare the results with those of actual experiment.

Detonation of Hydrogen and Oxygen at Constant Volume.

—Let us take a mixture of 2 volumes of hydrogen and 1 volume of oxygen, confined at atmospheric pressure, and a temperature of 0° C. , in a closed vessel, and cause it to deteriorate.

Theoretical Calculation, or Calculation of the Potential Elements.—This will be as follows:



Six volumes of the constituents give 4 volumes of final products.

$$\text{Heat} = 2 \times 57,632 = 115,264.$$

$$\text{Specific heat} = 2 \times 3 \times 2.422 = 14.532.$$

$$115,264$$

$$\frac{115,264}{14.532} = 9731.7^\circ \text{ C.}, \text{ potential increase of temperature.}$$

$$14.532$$

$$7931.7$$

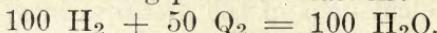
$$\frac{7931.7}{273} = 29.05 \text{ increase of pressure in atms.} \text{—products confined to their specific volume.}$$

The specific volume of the products being $\frac{2}{3}$ of the confining volume, the pressure is correspondingly reduced.

$$\frac{2}{3} \times 29.05 = 19.37 \text{ increase of pressure in atms.}$$

Calculation, allowing for Normal Dissociation of H₂O Molecules.—

Assume the following potential reaction:



Under normal triatomic dissociation we would have 59 H₂O dissociated into 59 H₂ + 29.5 O₂.

The heat developed will be

$$41 \text{ Q} = 41 \times 57,632 = 2,362,912 \text{ units.}$$

The specific heat of the products,

$$\begin{array}{l} 41 \text{ H}_2\text{O} = 41 \times 3 \times 2.422 \\ 59 \text{ H}_2 = 59 \times 2 \times 2.422 \\ 29.5 \text{ O}_2 = 29.5 \times 2 \times 2.422 \\ 2,362,912 \end{array} \left. \right| = 300 \times 2.422 = 726.6.$$

$$\frac{726.6}{3252^\circ} = 3252^\circ \text{ increase of temperature.}$$

$$\frac{3252^\circ}{273} = 11.91 \text{ increase of pressure in atms. at specific volume}$$

of products. The specific volume of the products is 86⅓ per cent. of the confining volume.

$$11.91 \times 0.8633 = 10.28 \text{ increase of pressure in atms.}$$

According to the classical experiments of Bunsen, who used a loaded valve to determine the pressure, the increase of pressure developed by the detonation of such a mixture of hydrogen and oxygen is 9.6 atmospheres. The later result, obtained by Berthelot and Vicille, with their registering gauge, is a little higher, 9.8 atmospheres (see Annales de Chimie et de Physique, 6^e serie, tom IV.), and I have no doubt this is very correct. The result calculated above, 10.28 atmospheres, by assuming normal dissociation of the H₂O molecules, is therefore a rough approximation.

*Calculation Assuming both Triatomic and Diatomic Dissociation.—*We cannot accept the result given above, because the exigencies of our theory require us to assume that there is also dissociation of the diatomic constituents H₂ and O₂, and this dissociation must be taken into account.

For the sake of simplicity we have assumed that the molecules H_2 and O_2 have the same heat of formation $Q^1 = \frac{Q}{1.5}$

in which Q is the heat of formation of H_2O .

According to our previous calculations the number of molecules of each class dissociated will be as follows:

$$\text{Triatomic, } n^{111} = 53.35.$$

$$\text{Diatomc, } n^{11} = 14.37.$$

The dissociated system (consisting of 200 atoms of hydrogen and 100 atoms of oxygen—total, 300 atoms) in the initial state of combination will be as follows:

$$m^{111} = 46.65 \text{ triatomic molecules} = 139.95 \text{ atoms}$$

$$m^{11} = 65.65 \text{ diatomic molecules} = 131.30 \text{ atoms}$$

$$m^1 = 28.75 \text{ monatomic molecules} = 28.75 \text{ atoms}$$

$$141.05 \qquad \qquad \qquad 300.00$$

$$\begin{aligned} \text{The heat rendered latent is } n^{111} Q &= 53.35 Q \\ n^{11} Q^1 &= 9.58 Q \end{aligned}$$

$$\text{Total . . . } 62.93 Q$$

The heat realised as active is therefore

$$100 Q - 62.93 Q = 37.07 \times 57,632 = 2,136,418 \text{ units.}$$

The specific heat of the dissociated system is as follows:

$$m^{111} = 46.65 \times 3 = 139.95$$

$$m^{11} = 65.65 \times 2 = 131.30$$

$$m^1 = 28.75 \times 1.23^* = 35.36$$

$$306.61 \times 2.422 = 742.61.$$

$$2,136,418$$

$$\frac{2,136,418}{742.61} = 2877^\circ \text{ increase of temperature.}$$

$$742.61$$

*The specific heat of a monatomic molecule is 0.615 of that of a diatomic molecule. The specific heat of an atom in the monatomic state is to its specific heat in the diatomic state as 1.23 : 1.

2877

$\frac{1}{273}$ = 10,538 atmospheres increase of pressure at specific volume.

The specific volume of the products is twice the number of molecules of all kinds in the dissociated system, and is equal to 282.10. The confining volume being 300, we have

282.10

$10.538 \times \frac{1}{300} = 9.91$ atms. increase of pressure.

The experimental increase of pressure being 9.8 atmospheres, this calculated result shows the right sort of agreement with it, in being slightly greater. We may suppose that there is a small loss of heat by communication to the containing vessel, and another slight loss, due to imperfection of the mixture of gases.

It would be too much to say that it is proved by this calculation that the heats of formation of H₂ and O₂ are equal, and that each is $\frac{2}{3}$ of the heat of formation of H₂O, since we would obtain the same result by considering Q¹ to be the compound mean of the heats of H₂ and O₂, two molecules of hydrogen being taken to one of oxygen. Nevertheless there is a certain

Q

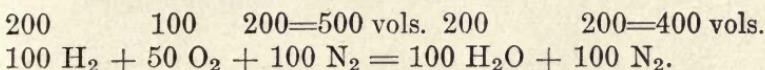
fitness in the ratio $\frac{Q}{Q^1} = 1\frac{1}{2}$, which makes it attractive.

Q¹

If we could apply the heat Q without loss to H₂O, at 0° C., we would produce H₂ + $\frac{1}{2}$ O₂ at the same temperature. The heat Q, rendered latent by breaking the triatomic molecule, appears to supply the energies for one and half diatomic. Since the total heat energies are not changed in the reaction, it is natural to suppose that Q, the heat of formation of the triatomic, is equal to $1\frac{1}{2}$ Q¹—Q¹ being equal to 38,421 units. If heat were the only form of energy concerned in the reaction, this reasoning would have great weight, but the mysterious form, chemical energy, plays a part, and being convertible into heat, may disturb these simple relations.

Hydrogen, Oxygen and Nitrogen.—To determine the effect of an admixture of a gas which takes no part in the

detonating reaction, we will next consider a mixture of hydrogen, oxygen and nitrogen, for which the potential reaction is as follows:



Theoretical Calculation.—This is as follows:

The potential heat

$$100 Q = 100 \times 57,632 = 5,763,200.$$

The specific heat is the total number of atoms (500) multiplied by the atomic heat $2.422 = 1211$ heat units. (This rule holds good when there are no monatomic gases present.)

$$\frac{5,763,200}{1211} = 4759^\circ \text{ C. potential temp.}$$

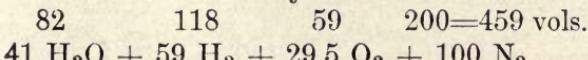
$$\frac{4759}{273} = 17.43 \text{ potential increase of pressure in atms. at specific volume.}$$

The specific volume of the products is $\frac{4}{5}$ of the confining volume, $17.43 \times \frac{4}{5} = 13.94$ increase of pressure in atms.

According to Berthelot and Vicille the actual increase of pressure for such a mixture is 8.75 atmospheres.

Normal Dissociation of H₂O Molecules.—The peculiarity of the present case is that if we suppose the dissociation to be confined to the H₂O molecules, and that this is normal (which, of course, is incorrect), we get a result which is much less than the observed increase of pressure. This is obviously due to the presence of the inert nitrogen, which shares the heat of the reaction with the components. The heat applied to the individual molecules is thereby lessened, and the dissociation of the H₂O falls far below the normal percentage. Nevertheless, for the sake of theory, we make the calculation.

The dissociated system will be as follows:



The heat will be $41 \times 57,632 = 2,362,912$.

The specific heat is not changed.

$$\frac{2,362,912}{1211} = 1951^{\circ}.$$

$$\frac{1951^{\circ}}{273} = 7.147 \text{ increased pressure in atms. at specific volume.}$$

The specific volume of the products is $\frac{459}{500}$ of the confining volume,

$$7.147 \times \frac{459}{500} = 6.56 \text{ atms.}$$

This is notably less than the experimental result 8.75 atmospheres, and may be taken as an indication that dissociation of the diatomic gases must be taken into account.

Dissociation of both Triatomic and Diatomic Molecules. —It is necessary to deduce formulas for this case. To simplify the problem we will assume that all the diatomic molecules, H₂, O₂ and N₂ have the same heat of formation, Q¹.

Our general formulas for dissociation are:

(1) For triatomic, n¹¹¹ = 0.59 Nh

$$(2) \text{ For diatomic, } n^{11} = \frac{Q}{Q^1} \text{ N}^1 h^1$$

(1) In the case of the triatomic gas the heat applied is 100 Q — n¹¹ Q¹, as before, but this heat is divided among 100 triatomic and 100 diatomic molecules (equal to 66½ triatomic), h is therefore

$$\frac{100 Q - n^{11} Q^1}{166.6}, \text{ and } Nh = \frac{100}{166.6} (100 Q - N^{11} Q^1).$$

Substituting this in the value of n^{111} above, we have

$$n^{111} = 0.354 \frac{(100 Q - N^1 Q^1)}{Q} \quad (a)$$

(2) In the case of the diatomic gases, the number of molecules to be considered is $N^1 = 250 - 1.5 m^{111}$ (m^{111} being the number of integral triatomic molecules in the dissociated system).

The heat applied is $100 Q - n^{111} Q = m^{111} Q$. This is divided between N^1 diatomic and m^{111} triatomic ($= 1.5 m^{111}$ diatomic). $N^1 + 1.5 m^{111} = 250$. The heat h^1 applied to each

diatomic molecule is therefore $\frac{m^{111} Q}{250}$, and we have

$$n^{11} = \frac{0.385 N^1 m^{111} Q}{250 Q^1}$$

Substituting the value of $N^1 = 250 - 1.5 m^{111}$, we have
 $n^{11} Q^1 = 0.00154 (250 m^{111} - 1.5 m^{111^2}) Q$ (b)

and this, in equation (a), above, gives

$$n^{111} = 0.354 (100 - 0.385 m^{111} + 0.00231 m^{111^2}),$$

whence n^{111} being equal to $100 - m^{111}$, we have

$$m^{111} = 70.14$$

$$n^{111} = 29.86$$

This value of m^{111} in equation (a) gives for the latent heat of the diatomic dissociation

$$n^{11} Q^1 = 15.54 Q \quad (c).$$

Taking the value of Q^1 such that $\frac{Q}{Q^1} = 1.5$, we have

$$n^{11} = 23.31.$$

The dissociated system of 500 atoms will be as follows:
 $m^{111} = 70.14$ no. integral triatomic molecules = 210.42 atoms
 $m^{11} = 121.48$ no. integral diatomic molecules = 242.96 atoms
 $m^1 = 46.62$ no. monatomic molecules = 46.62 atoms

$n^{111} = 29.86$ no. triatomic molecules dissociated
 $n^{11} = 23.31$ no. diatomic molecules dissociated.

The heat rendered latent is $n^{111} Q = 29.86 Q$
 $n^{11} Q^1 = 15.54 Q$

$$\text{Total . . } \overline{45.40} Q$$

The active heat is, therefore,
 $54.60 \times 57,632 = 3,146,707$ units.

The specific heat is as follows:

$$m^{111} = 70.14 \times 3 = 210.42$$

$$m^{11} = 121.48 \times 2 = 242.96$$

$$m^1 = 46.62 \times 1.23 = 57.34$$

$$\overline{510.72 \times 2.422 = 1236.96.}$$

$$\frac{3,146,707}{1236.96} = 2543.9^\circ \text{ C.}$$

$$\frac{2543.9}{273} = 9.318 \text{ atms. (at specific volume).}$$

The specific volume of the dissociated system is twice the total number of molecules, and is equal to 476.48.

$$\frac{476.48}{9.318 \times 500} = 8.88 \text{ atms. increase of pressure.}$$

The observed pressure being 8.75 atmospheres, this is a very close approximation, and of the right sort.

In the foregoing calculations we have virtually assumed that the heats of formation of the diatomic molecules, H_2 , O_2 and N_2 are the same. Of course, we have no proof that this is exactly true. We can draw certain inferences in regard to this from the experiments of Berthelot and Vicille. They make various admixtures of these three gases to the detonating mixture of hydrogen and oxygen, just capable of forming H_2O , and found the increase of pressure as follows (see Annalis de Chimie et de Physique, 6^e Serie tom IV.).

Table of Pressures for Mixtures.

	$H_2 + O$.	9.80 atmospheres
(2)	$H_2 + O + H_2 \dots \dots \dots$	8.82
	$H_2 + O + N_2 \dots \dots \dots$	8.75*
	$H_2 + O + O_2 \dots \dots \dots$	8.69
(3)	$H_2 + O + 3H_2 \dots \dots \dots$	7.06
	$H_2 + O + 3N_2 \dots \dots \dots$	6.89
	$H_2 + O + 3O_2 \dots \dots \dots$	6.78

It appears from this table that the admixture of equal volumes of hydrogen or oxygen or nitrogen to the detonating mixture of hydrogen and oxygen gives nearly the same effect in reducing the pressure. Of the three admixtures, hydrogen gives the highest resulting pressure, oxygen gives the lowest, and nitrogen very nearly a mean between the two. It is easy to show from our formulas that the resulting pressure is the greater the less the heat of formation of the added gas. For

Q

instance, in regard to the mixture of H_2 and O, assuming — Q¹

= 1½, we found the increase of pressure* 9.92 atmospheres. Q¹

If — = 2, the pressure would be about 10.2 atmospheres. Q¹

Interpreting the table above, we might conclude, therefore, that the heats of formation of the three diatomic gases are approximately equal, but that of oxygen is the highest, hydrogen the lowest, and nitrogen intermediate.

However, such a deduction is uncalled for, since the slight discrepancy can be explained in a simpler way. At ordinary

*My calculated pressure for this mixture applies to the group, since I have taken the heats of formation of H_2 , N_2 , and O_2 equal. It is very satisfactory to note that my result, 8.88, shows a very close agreement when the admixture is hydrogen, and an agreement of the right kind.

*We sometimes speak of the *pressure* and sometimes of the *increase of pressure*, meaning the same thing. Both expressions are admissible, provided the matter is understood. The detonating gaseous mixture being already under a pressure of one atmosphere, the gauge indicates the pressure due to the explosion, or the increase above one atmosphere.

temperatures, hydrogen is the most perfect gas of the three, and oxygen the most imperfect. The internal work expended in bringing these gases to the temperature at which they obey the laws of gases with accuracy—a work which means a corresponding loss in the Kinetic energy realised—is slight for all three, but least in the case of hydrogen, and greatest in the case of oxygen.

For the cases given in group (3) of the table, where 6 volumes of an inert or surplus gas are added to 3 volumes of the normal detonating mixture of hydrogen and oxygen, we have made the usual calculations, but only give the summaries.

(1) Assuming that there is no dissociation, the potential elements are as follows:

Temperature, 2974° ; pressure, 9.63 atmospheres.

(2) Normal dissociation of the H_2O ,

Temperature, 1084° ; pressure, 3.79 atmospheres.

(3) Dissociation of both triatomic and diatomic gases,
Temperature, 1597° ; pressure, 5.76 atmospheres.

The dissociated system for assumption (3) is as follows:

Dissociated $n^{111} = 15.06$

molecules $n^{11} = 35.16$

$m^{111} = 84.94$. The total number of atoms is
900.

Integral $\left\{ \begin{array}{l} m^{11} = 287.43. \quad \text{The total number of atomic} \\ m^1 = 70.32. \quad \text{heats, } 916.17. \end{array} \right.$
molecules

K_v , the specific heat, is 2218.96.

The heat rendered latent, $n^{111} Q = 15.06 Q$

$n^{11} Q^1 = 35.16 = 23.44 Q$

Total .. $1\frac{1}{2}$

 38.50 Q

The active heat is 61.50 Q.

This case is specially interesting, in giving apparently a failing case for our formulas. According to these, assuming dissociation for both triatomic and diatomic gases, the temperature reached is only 1597° C., and the pressure is 5.76 atmo-

spheres—corresponding to an active heat of 61.50 Q—the heat rendered latent being 38.50 Q.

The experimental pressure for the admixture of hydrogen (the most perfect gas) was 7.06 atmospheres. We can work backward from this, and get approximate values for the other elements, viz., temperature, 1940° C. (instead of about 1600°), an active heat 75.00 Q (instead of 61.50), and for the heat rendered latent the equivalent of 25 triatomic molecules (instead of 38.50).

It is evident that in the case of this mixture our formulas give over-estimates of the effects of dissociation, in fact, they do not give accurate values for the pressures when the percentage of inert gas added is very large (in this case three times the volume of the main product, or twice the volume of the components). Supposing the principle of the formulas to be sound, and that no error has been made in applying them to this mixture, we will call the values of n^{111} and n^{11} the theoretical percentages of dissociation, and 5.76 atmospheres the theoretical increase of pressure, which is only 81.6 per cent. of that determined practically.

The principle of the formulas (which is more easily stated than applied) is as follows: When a confined mixture of gases undergoes a detonation by virtue of a chemical reaction between a portion of them, the resulting dissociation in each gas is fixed by this relation—the heat rendered latent by dissociation bears the same ratio to the total heat applied to the gas that the internal energy bears to the whole energy of the molecule.

Our theory is really based upon a succession of reactions, ending in a final equilibrium. To show this, we give the reasoning followed in the calculations. The primary heat, to be considered as applied to the gaseous mixture, is the potential heat of 100 molecules of $H_2O = 100$ Q. But this is applied not only to the triatomic gas and its components, but to the 300 diatomic molecules of surplus or inert gas, the whole being the heat equivalent of 300 triatomic molecules. Each of the triatomic molecules is therefore considered subjected to a heat $= \frac{1}{3}$ Q, but this will produce enough heat to dissociate some of the diatomic molecules, and render latent a quantity of heat

$n^{11} Q^1$, so that the final heat to be taken as applied to each molecule of the triatomic system is

$$\frac{n^{11} Q^1}{\frac{1}{3} Q} = \frac{n^{11} Q}{300}, \text{ equal by hypothesis to } \frac{1}{3} Q = \frac{n^{11} Q}{450}$$

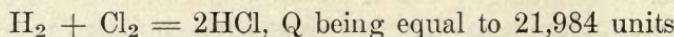
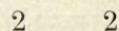
The heat considered as applied to the diatomic system is the active heat, $m^{111} Q$ of the dissociated triatomic system. The number of diatomic molecules in the mixture is 300, but the heat being divided between these and the triatomic, the diatomic system must be taken equal to 450 molecules, and

$$\text{the heat } h^1 \text{ applied to each molecule is therefore } \frac{m^{111} Q}{450}.$$

I need not go further with the analysis, since I have already given the details for an analogous but simple case, but it is natural to think that in a mixture where these complicated heat reactions obtain that the system will be one of fluctuating composition and decomposition, even during the minute interval of time covered by the detonation, and that short as this period is, it will include a number of different stages before the system settles into equilibrium.

The state of equilibrium which we calculate from our formulas is the theoretical; that is, the state of equilibrium before there is any loss of the potential heat of the system. The detonation is propagated by a wave of high velocity, so that the reaction may be taken as beginning simultaneously in all parts of the containing vessel. If in any stage preceding the state of equilibrium, the dissociation is less than the theoretical, the pressure recorded, which is the maximum, will be greater than the theoretical.

Hydrogen and Chlorine.—Our next case is a mixture of equal volumes of hydrogen and chlorine. The chemical equation and theoretical calculation are as follows:



The heat is $2HCl = 2 \times 21,984 = 43,968$ units.

The specific heat = $4 \times 2.422 = 9.688$.

43,968

 $\frac{43,968}{273} = 16.62$ increase of pressure in atms.

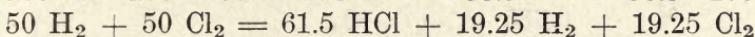
9.688

4538.4

 $\frac{4538.4}{273} = 16.62$ increase of pressure in atms.

This is the theoretical increase of pressure since the products are confined at specific volume.

Normal Dissociation of HCl.—If we suppose the dissociation to be confined to the diatomic hydrogen-chloride (into diatomic hydrogen and chlorine), and that this is normal, then 38.5 per cent. of the HCl will be dissociated, and for a total of 100 diatomic molecules the reaction would be as follows:



The active heat will be

$$61.5 \times 21,984 = 1,352,016.$$

$$\text{The specific heat} = 200 \times 2.422 = 484.4.$$

$$1,352,016$$

 $\frac{1,352,016}{273} = 2791^\circ \text{ C. increase of temperature t.}$

484.4

2791

 $\frac{2791}{273} = 10.22$ atmospheres.

273

(Both temperature and pressure are 61.5 per cent. of the theoretical.)

Dissociation of HCl, H₂ and Cl₂.—Though the result given above may be approximately correct, we cannot accept it. According to our theory the diatomic gases H₂ and Cl₂ are also subject to a certain amount of dissociation.

It must be kept in mind that we are considering the dissociation of the three diatomic gases HCl, H₂ and Cl₂, the potential heat being the heat of formation of 100 HCl from 50 H₂ and 50 Cl₂, and not from 100 H and 100 Cl. Q₁ the heat of formation of HCl from $\frac{1}{2}$ H₂ + $\frac{1}{2}$ Cl₂ = 21,984 units of heat. For simplicity, assume that H₂ and Cl₂ have the same heat of formation Q¹ from their monatomic constituents.

Our general formulas for dissociation are:

$$0.385 \text{ Nh}$$

$$(1) \text{ For HCl molecules, } n_{11} = \frac{0.385}{Q_1} (m_{11} = 100 - n_{11}).$$

$$(2) \text{ For H}_2 \text{ and Cl}_2 \text{ molecules } n^{11} = \frac{0.385}{Q^1} N^1 h^1$$

In case (1) we have $N = 100$ and $h = 100 Q_1 - n^{11} Q^1$,
 $(100 Q_1 - n^{11} Q^1)$

$$\text{whence } n_{11} = 0.385 \frac{Q_1}{Q_1} \quad (\text{a})$$

$$\text{For case (2) we have } N^1 = n_{11} \quad h^1 = \frac{m_{11} Q_1}{100}$$

$$n^{11} = \frac{0.385 n_{11} m_{11} Q_1}{100 Q^1} \quad (\text{b})$$

Substituting $n_{11} = 100 - m_{11}$ in this we have

$$n^{11} Q^1 = 0.385 m_{11} Q_1 - 0.00385 m_{11}^2 Q_1$$

And this, in equation (a) gives

$$100 - m_{11} = 38.5 - 0.148225 m_{11} + 0.00148225 m_{11}^2,$$

whence

$$m_{11} = 64.88$$

$$n_{11} = 35.12$$

$$n^{11} = 8.77 \frac{Q_1}{Q^1}$$

Taking $Q^1 = 38,421$ heat units ($\frac{2}{3}$ 57,632 the heat Q for the H_2O molecules), we have

$$\frac{Q_1}{Q^1} = \frac{21,984}{38,421}, \text{ and } n^{11} = 5.02.$$

$$\text{The heat rendered latent will be } n_{11} \frac{Q_1}{Q_1} = 35.12 \frac{Q_1}{Q_1}$$

$$n^{11} \frac{Q_1}{Q^1} = 8.77 \frac{Q_1}{Q_1}$$

$$\frac{43.89}{Q_1} Q_1$$

The active heat will be

$$56.11 Q_1 = 56.11 \times 21,894 = 1,233,522$$

The specific heat can be calculated from the dissociated system as follows:

$$m_{11} = 64.88 \times 2 \quad (\text{HCl}) \quad = 129.76 \text{ atomic heat units, } 129.76 \text{ atoms.}$$

$$m^{11} = 30.10 \times 2 \quad (\text{H}_2 + \text{Cl}_2) = 60.20 \text{ atomic heat units, } 62.20 \text{ atoms.}$$

$$m^1 = 10.04 \times 1.23 \quad (\text{H} + \text{Cl}) = 12.35 \text{ atomic heat units, } 10.04 \text{ atoms.}$$

$$\text{Specific heat, } 202.31 \times 2.422 = 489.99.$$

$$\frac{1,233,522}{489.99} = 2517.4^\circ \text{ C.} = t.$$

$$\frac{2517.4}{273} = 9.22 \text{ atms. at specific volume.}$$

The specific volume of the products (twice the total number of molecules in the dissociated system) is 210.04. The confining volume is 200.

$$9.22 \times \frac{210.04}{200} = 9.68 \text{ atms.}$$

Berthelot and Vicille did not include a mixture of hydrogen and chlorine in the tables to which I have had access, so that we have no accurate experimental data with which to compare this result. However, Mallard and Le Chatelier (see table, page 391, "Explosives and Their Power") determined the pressure for a detonating mixture of hydrogen and chlorine, using a hollow metallic spring as a manometer. The mixture was not pure; it contained 95 per cent. (by volume) of the detonating mixture, 3 per cent. of surplus hydrogen, and 2 per cent. of water vapour. They obtained for the pressure 8.1 atmospheres.

We can get a rough idea of the diminution of the pressure due to the presence of inert gases, by comparing certain other results given in the same table with the increase of pressure

in atmospheres obtained by Berthelot and Vicille, working upon pure mixtures, thus:

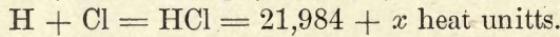
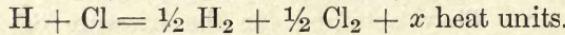
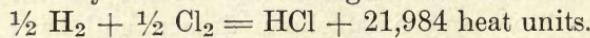
	B. & V.
Mallard and Le Chatelier's Mixture. M & L. Pure Mixt.	Diff.
0.94 (CO + O) + 0.06 nitrogen and	
water vapour	8.6 10.12 1.52
0.955 (H ₂ + O) + 0.03 N + 0.015	
water vapour	9.2 9.8 0.60

It also appears from the table that water vapour has a greater effect in diminishing the pressure than either hydrogen or nitrogen, which, of course, agrees with theory, its internal energy being greater.

As a rough estimate we take the increase of pressure for the pure HCl mixture to be 9.3 atmospheres, or 1.20 greater than found for the impure mixture.

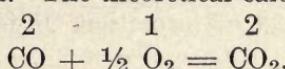
Our calculated result 9.69 is quite as close as could be expected. Chlorine being a very imperfect gas, will absorb energy which the theory does not take into account (see footnote on page — of this chapter). If we had data showing the relative effects of adding H₂ or Cl₂ to a mixture already in HCl proportions, this fact would doubtless be brought out very clearly. In fact, in one of Berthelot's papers I have seen some comments upon the difference in the effect of adding surplus chlorine or surplus hydrogen, but have not been able to find the record of the experiments.

In the calculation it will be noticed that Q¹ is greater than Q₁, the latter being 21,984—the heat of formation of hydrogen chlorine from diatomic hydrogen and chlorine—or, we may consider this the difference between the heat of formation of HCl from diatomic hydrogen and chlorine, and its heat of formation from these elements taken as monatomic. Thus we may write the following thermal relations:



We have supposed the heats of formation of hydrogen and chlorine to be equal, and have taken x = 38,421 heat units. According to this supposition, the heat of formation of HCl from monatomic constituents is 60,405 units.

Carbonic Oxide and Oxygen.—We will attempt to treat this case in the usual way, but, as will be presently seen, it has difficulties of its own. The theoretical calculation is as follows:



The heat is 96,960 (the heat of formation of CO_2) less 29,290 (the heat of formation of CO) = 67,670.

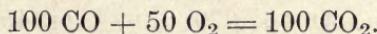
$$\begin{array}{r} \text{The specific heat} = 3 \times 2.422 = 7.266. \\ 67.670 \\ \hline 7.266 = 9313.2^\circ \text{ C. theoretical temperature} = t. \end{array}$$

$$\begin{array}{r} 9313.2 \\ \hline 273 = 34.11 \text{ atms. (at specific volume).} \end{array}$$

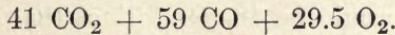
The specific volume of the products being $\frac{2}{3}$ of the confining volume, we have

$$\frac{2}{3} \times 34.11 = 22.74 \text{ atms. theoretical increase of pressure.}$$

Normal Dissociation of CO_2 .—Let the potential reaction be



The normal dissociation of CO_2 being 59 per cent., we have as products



$$\text{The heat} = 41 \times 67,670 = 2,774,470.$$

The specific heat is not changed by this dissociation.

$$\begin{array}{r} 2,774,470 \\ \hline 726.6 = 3818.4^\circ \text{ C.} = t. \end{array}$$

$$\begin{array}{r} 3818.4 \\ \hline 273 = 13.987 \text{ atms. (products at specific volume).} \end{array}$$

The specific volume of the products is $86\frac{1}{3}$ per cent. of the confining volume.

$$13,987 \times 0.8633 = 12.08 \text{ atms. increase of pressure.}$$

Dissociation of CO₂, CO and O₂.—Let us assume, as in the case of the detonating mixture of hydrogen and oxygen, that the dissociation involves the diatomic constituents (CO and O₂), and that the heat of formation Q¹ is the same for both.

Q

If we also assume that $\frac{Q}{Q^1} = 1\frac{1}{2}$, our formulas become the

same as in the parallel case of H₂O, H₂ and O₂. Then, for 100 possible molecules of CO₂, we have

n¹¹¹ = 53.35, and the latent heat 53.35 Q

n¹¹ = 14.37, and the latent heat 9.58 Q

62.93 Q

Making the calculation as before, but taking Q = 67,670, we find the temperature 3378°, and the increase of pressure 11.64 atms.

The latest determination of the pressure by Berthelot and Vicille is 10.12 atms., so that this result is considerably too high.

The result, 11.64 atmospheres, is obtained by a routine calculation, in which we virtually assume that the compound mean of the heats of formation of O₂ and CO (two of the latter to one of the former) is $\frac{2}{3}$ of the heat of formation of CO₂ from CO and O (67,670 units), or 45,113 heat units, whereas in our former calculations we have taken Q¹ for the elementary diatomic gases equal to 38,421. If this be correct, then Q¹ for CO would be 48,459. Since the observed heat of CO from amorphous carbon and gaseous O₂ is 29,290, this would allow 19,169 units expended in gasifying the carbon. But in the case of HCl, to which CO is somewhat analogous, we found Q¹ 21,984 units greater than Q¹ for each of its constituents—a case in which there is no heat expended in change of state; it is therefore likely that the real heat of CO is considerably greater than 48,459, which puts in doubt the percentage of dissociation, and the correctness of our calculation.

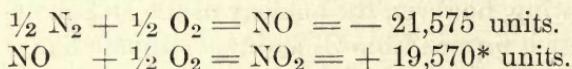
Dissociation of CO₂, CO, O₂ and C₂ under Thomsen's Hypothesis.—It is reasonable to suppose that if the molecule CO is dissociated it must be at a temperature above the boiling

point of carbon. We can reason that when the molecule is decomposed the carbon must be left at least for the instant in the state of separate atoms, or as a monatomic gas, so that we may consider the CO formed from gaseous monatomic oxygen and carbon. Following, however, the analogy of the HCl molecule, we will consider it formed from C₂ and O₂, without change of volume. Its heat of formation from *solid* amorphous carbon is 29,290 heat units. To this must be added the heat necessary to gasify the carbon. Thomsen, the great Danish thermo-chemist, has suggested that this additional heat is 38,380 units, so that the real heat of formation of CO from its diatomic gaseous constituents is the same as CO₂ from CO and ½ O₂, viz., 67,670.

Parenthetically, we may say that three forms of solid carbon are recognised by the thermochemists—the diamond, graphite and amorphous carbon (or pure charcoal). The amorphous is the simplest form, but in all the molecule is probably complex, while in the diamond and graphite there are also probably forces of great magnitude giving rise to cohesion between the molecules. The heat of formation of a compound from amorphous carbon is always greater than its heat from carbon taken as graphite or diamond. Berthelot always takes it as diamond, and his heats of formation are generally lower than Thomsen's, who takes it as amorphous. Thus the value of Q for CO₂ from amorphous carbon is 96,960 units (Faure and Silbermann's determination), while Berthelot's value is 94,310.

Thomsen's hypothesis in regard to the true heat of formation of CO from gaseous carbon is founded upon the assumption of a "constant of oxidation" for each added atom of oxygen, making the heat CO + O, the same as C + O. While this idea is supported by many facts in thermochemistry, there seem to be marked exceptions. Moreover, there is *a priori* reasoning, which can be brought against it. One case is an oxidation of carbon alone, the other the oxidation of carbon and oxygen, the combined attraction of which (supposing this to measure the energy of union with oxygen) may be greater than that of carbon alone.

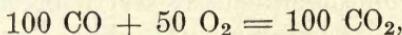
For instance, if we consider nitrogen in the place of carbon, and thus get rid of the complication of the change of state, since both the elements and the products may be taken as gases, we have



The heat of formation of NO_2 from diatomic oxygen and nitrogen is therefore 41,145 units greater than that of NO from the same elements. There is no constant of oxidation here.

But while this casts doubt upon Thomsen's hypothesis, it is not a strong argument that his real heat of formation for CO is too high. In reactions of this kind, the mystery called "elective affinity" comes into play, and obscures the conclusions otherwise obvious. The first reaction given above simply means that the average heat of formation of N_2 and O_2 exceeds that of NO (from diatomic constituents) by 21,575 units (a contrary case to that of HCl), which again implies that the "elective affinity" between monatomic N and O is relatively weak, whereas between C and O we know it is very strong. It is therefore possible that Thomsen's value for the heat expended in gasifying carbon may be too low instead of too high.

Applying Thomsen's hypothesis, that the heat of formation of CO from C_2 and O_2 is equal to 67,670, to the system



we must consider the dissociation of CO separately from the elementary gases C_2 and O_2 .

Let Q be the heat of formation of CO_2 from CO and diatomic O = 67,670 units.

Let Q^{11} be the heat of formation of CO from diatomic C and O = 67,670 units.

Let Q_{11} be the heat of formation of C_2 and O_2 (supposed equal for convenience), from monatomic C and O, respectively = 38,421 units.

*Part of this heat is due to polymerisation—the gas at ordinary temperature consists of a mixture of NO_2 and N_2O_4 .

The general formulas and substituted values are as follows:

$$\text{For dissociation of CO}_2 \quad n^{111} = \frac{0.59 \text{ Nh}}{Q}, \quad N = 100, h =$$

$$\frac{100 Q - n^{11} Q^{11}}{100} - n_{11} Q_{11}.$$

$$\text{For dissociation of CO} \quad n^{11} = \frac{0.385 \text{ N}^1 \text{h}^1}{Q^{11}}, \quad N^1 = n^{111}, h^1 =$$

$$\frac{m^{111} Q - n_{11} Q_{11}}{150}.$$

$$\text{For dissociation of C}_2 + \text{O}_2, \quad n_{11} = \frac{0.385 \text{ N}^{11} \text{h}^{11}}{Q_{11}}, \quad N^{11} =$$

$$\frac{\frac{1}{2} n^{111} + n^{11}, h^{11}}{150} = \frac{m^{111} Q - n^{11} Q^{11}}{150}$$

$$\begin{aligned} n^{111} Q &= 0.59 (100 Q - n^{11} Q^{11} - n_{11} Q_{11}) & Q = Q^{11} = 67670 \\ &0.385 n^{111} (m^{111} Q - n_{11} Q_{11}) \\ n^{11} Q^{11} &= \frac{n^{111} Q^{11}}{150} & Q_{11} = 38421 \\ &\frac{Q}{Q_{11}} = \frac{1}{150} & Q = \frac{1}{38421} \times 67670 = 17613 \end{aligned}$$

$$n_{11} Q_{11} = \frac{0.385 (\frac{1}{2} m^{111} + n^{11}) (m^{111} Q - n^{11} Q^{11})}{150}$$

whence

$$n^{111} = 59 - 0.59 n^{11} - 0.335 n_{11}$$

$$n^{11} = 0.002567 n^{111} m^{111} - 0.001457 n^{111} n_{11}$$

$$n_{11} = 0.00452 (\frac{1}{2} n^{111} m^{111} + n^{11} m^{111} - \frac{1}{2} n^{111} n^{11} - n^{112})$$

These equations are satisfied by the values—

$$n^{111} = 53.51$$

$$n^{11} = 5.92$$

$$n_{11} = 5.99$$

But there must be some error in the hypothesis, since n_{11} cannot exceed n^{11} —that is, the dissociation of C_2 and O_2 cannot exceed the number of molecules of these set free by the dissociation of the CO. This error may lie in assigning too great a value to the heat Q^{11} , or too low a value to Q_{11} —probably the latter.

The difference between n^{11} and n_{11} being small, we take both equal to 5.92.

The heat rendered latent will be

$$\begin{array}{rcl} n^{111} Q & = & 53.51 Q \\ n^{11} Q^{11} & = & 5.92 Q \\ n_{11} Q_{11} = 5.92 Q_{11} & = & 3.36 Q \\ \hline & & \\ 1.7613 & & 62.79 \end{array}$$

The active heat is $37.21 \times 67,670 = 2,518,001$.

The specific heat of the dissociated system is found as follows:

	atomic heats		
$m^{111} = 46.49$	$CO_2 \times 3$	139.47	139.47 atoms
$m^{11} = \left\{ \begin{array}{l} 47.59 \text{ CO} \times 2 \\ 26.755 \text{ O}_2 \times 2 \end{array} \right.$		95.18 } 53.51 }	148.69 atoms
$m^1 = \left\{ \begin{array}{l} 5.92 \text{ O} \\ 5.92 \text{ C} \end{array} \right\}$	11.84×1.23	14.56	11.84 atoms
		132.675	302.72 300.00 atoms
$302.72 \times 2.422 = 733.19 = K_v$			
$2,518,001$		3434	
$\frac{733.19}{2,518,001} = 3434^\circ \text{ C.} = t.$	$\frac{3434}{273} = 12.58$		atmospheres at
			273
	specific volume.		

The specific volume is twice the number of molecules in the dissociated system, and equal to 265.35.

$$12.58 \times \frac{265.35}{300} = 11.13 \text{ atms.}$$

The experimental result being 10.12, this pressure is about 1 atmosphere too great.

This is the closest approximation to the experimental result we have been able to obtain by any calculation based strictly upon the laws of gases. We have supposed the temperature attained to be above the boiling point of carbon. This is necessary in order to bring the case within these laws. We may suppose CO to be dissociated into solid carbon and gaseous oxygen, but this, besides being (under the conditions) a violation of the law of maximum free energy, is not dissociation within the meaning of our formulas.

We can also suppose that the CO does not suffer dissociation, the boiling point of carbon being higher than the temperature attained. This does not seem probable, in view of the temperature, which we know to approximate 3800° C., if the CO is not decomposed.

However, this supposition is negatived, because it gives a still greater value for the pressure than the one above.

Our calculation is not satisfactory, however, in embracing several improved hypothesis. Besides assuming a constant heat of formation for elementary gases, we have considered gaseous carbon as *diatomic*, and assigned it the same heat of formation as O₂, H₂, N₂, etc. We have also taken the heat of formation of CO from its constituents as 67,670 units, or the same as CO₂ from CO and O₂. This last proposition is supported by the greatest of the thermochemists, but after all it is an hypothesis.

Accepting the calculation as approximately correct, the most probable explanation for the discrepancy between the calculated result and that obtained by experiment is this. While carbon is set free as a gas, by the dissociation of the carbonic oxide, its point of volatilisation is so high that it does not obey the laws of gases accurately. Its specific heat is probably higher than that allowed for in the calculation, while its specific volume

is less. Either change in the figures would tend to lessen the calculated pressure. This brings the case within the general rule for imperfect gases.

To complete this chapter, we compile a table for different detonating gaseous mixtures, comparing our calculations of the pressure (under the two assumptions as to the dissociation) with the experimental determinations of the pressure.

Table—Detonating Gaseous Mixtures—Pressures in Atmospheres.

Detonating Mixture.	Final Product.	Theoretical or Potential Pressure.	Calculated Pressure allowing for			Difference between 5 and 6.	Percentage ratio of Experimental to Theoretical Pressure, 6:3
			Dissociation of Main Product.	Dissociation of Diatomic Constituents also.	Actual Pressure by Experimental Determination.		
1	2	3	4	5	6	7	8
$H_2 + \frac{1}{2}O_2$	H_2O	19.37	10.28	9.91	9.80	0.11	50.6
$H_2 + \frac{1}{2}O_2 + H_2$	$H_2O + H_2$	13.94	6.56	8.88	8.82	0.06	63.3
$H_2 + \frac{1}{2}O_2 + N_2$	$H_2O + N_2$	"	"	"	8.75	0.13	62.8
$H_2 + \frac{1}{2}O_2 + O_2$	$H_2O + O_2$	"	"	"	8.69	0.19	62.2
$H_2 + Cl_2$	$2HCl$	16.62	10.22	9.68	? 9.30	? 0.38	? 56.0
$CO + \frac{1}{2}O_2$	CO_2	22.74	12.08	11.13	10.12	1.01	44.5
$H_2 + \frac{1}{2}O_2 + 3H_2$	$H_2O + 3H_2$	9.68	3.79	5.76	7.06	-1.30	72.7
$H_2 + \frac{1}{2}O_2 + 3N_2$	$H_2O + 3N_2$	"	"	"	6.89	-1.13	71.2
$H_2 + \frac{1}{2}O_2 + O_2$	$H_2O + O_2$	"	"	"	6.78	-1.02	70.0

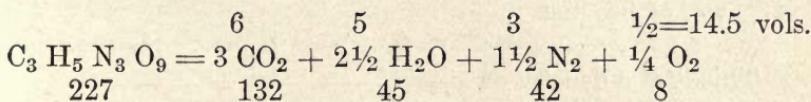
CHAPTER XII.

Dissociation in Explosives.—Specific Heats.—Boyle's Law at High Densities.

Dissociation in Explosion Products.—Nitroglycerine as Illustration.—General Principles.—Estimates of Dissociation in N.G. Products.—Mercury Fulminate.—Dissociation of its Products.—Question of Specific Heats.—Not Increased at Explosion Temperature.—Boyle's Law at High Densities.—Isothermals of a Perfect Gas.—Isothermals of an Imperfect Gas.—Isothermals of Hydrogen.—Improvement with Temperature.—Increase of Pv at High Densities.—Experimental Evidence.—Pressures of Explosives at Absolute Densities.

Dissociation in Explosion Products.—Dissociation accompanying the detonation of gaseous mixtures has been treated in the preceding chapter. When one attempts to apply the same course of reasoning to the products of solid or liquid explosive bodies, he encounters certain difficulties.

Nitroglycerine as Illustration.—We take the case of nitroglycerine as an example. The metamorphosis may be represented as follows:



In calculating the heat of decomposition H (products taken as gaseous), we use the data of McNab and Ristori.

$$\begin{array}{rcl} 3 \text{ CO}_2 & = & 3 \times 96,960 = 290,880 \text{ heat units} \\ 2\frac{1}{2} \text{ H}_2\text{O} & = & 2\frac{1}{2} \times 57,632 = 144,080 \text{ heat units} \end{array}$$

434,960

Deduct heat of formation of N.G. 86,606

H — heat of decomposition for
227 units = 348,354 heat units

The final products, as shown above, consist of:

Triatomic molecules	5½
Diatomie molecules	1¾
Total	7¼

About 76 per cent. of the products by volume are therefore triatomic.

227 British Criths = $227 \times .005592 = 1.2694$ pounds, give 14.50 cubic feet.

1 pound gives 11.423 cubic feet = V specific vol.

Potential Elements.—We first calculate the potential temperature and pressure.

The specific heat is as follows:

$$\text{Triatomic molecules } 5\frac{1}{2} \times 3 = 16.50$$

$$\text{Diatomie molecules } 1\frac{3}{4} \times 2 = 3.50$$

$$20.00 \times 2.422 = 48.44 = K_v$$

$$H \quad 348,354$$

$$\frac{H}{K_v} = \frac{348,354}{48.44} = 7191.45^\circ C = t \text{ potential rise of temperature.}$$

$$K_v \quad 48.44$$

$$7191.45^\circ + 273^\circ = 7464.45^\circ = T \text{ potential absolute temperature.}$$

$$7464.45^\circ$$

$$\frac{7464.45^\circ}{273} = 27.342 \text{ atmospheres—potential pressures at spec.}$$

$$273$$

vol. of products.

$$\text{This is at a density of } \frac{1}{62.425 \times 11.423} = \frac{1}{713.07}$$

At unit density the pressure is $27.342 \times 713.07 = 19,497$ atmospheres.

At absolute density of nitro-glycerine (1.60) the pressure = 31,195 atmospheres.

General Principles.—To estimate the dissociation, we apply as well as we can the principles developed in the last chapter, relating to the dissociation in detonating gaseous mixtures. It must be kept in mind that the heat applied, H, is not the heat of formation of the gaseous products from gaseous constituents,

but this, less the heat of formation of the explosive itself, the same elements* being considered in the two cases.

The heat of formation to be considered for each gas is the heat of formation under the conditions, from the assumed products of its dissociation.

The heat applied is the total heat H , apportioned to each gas according to its specific heat.

Besides the development of heat as such represented by H , there is a certain amount of energy developed represented by that of the gaseous products in their final standard state (this state is theoretical so far as the H_2O is concerned). The two energies added together, being first reduced to the same terms, make up the potential of the explosive. It is easy to calculate this additional energy in heat terms, viz., 13,224 heat units equal to $K_v \times 273$. But it does not seem that we are concerned with this heat, since in our consideration of dissociation we take both the primitive system and the dissociated system as being in the gaseous state.

The metamorphosis of an explosive body may be conveniently considered in three stages: (1) the quiescent explosive; (2) the initial state of the products in the explosive reaction (this is the dissociated state of the system); (3) the final state of the system, when the products have been cooled to the standard temperature, and have taken their stable form.

Our object is to find (2) the initial state of combination of the products. As data, we have the final state of the system (3), and the heat H given out in passing from (1) to (3).

The potential or total energy of the explosive is equal to the energy in the final state (3), plus the heat given out.

*When the elements from which a compound is formed are not stated, it is generally understood that they are taken in their ordinary state. The heat of formation of nitro-glycerine 86,606 is from amorphous carbon and gaseous diatomic nitrogen, hydrogen and oxygen. It does not alter the heat of decomposition H , if we take the carbon as diamond, since the heat of the products and the heat of formation of the explosive are affected alike. The heat of decomposition H , in fact, is the thing determined practically in the calorimeter, and the other is obtained by fixing a quantity which, subtracted from the known heat of the products, will give the heat H .

In the explosive body (1) the whole energy is potential. In state (2), part of the energy is potential (that is, latent for the time being), and part active.

In state (3) none of the energy is potential or latent; a small part is active, but the great portion H has been lost by communication as heat to other bodies.

Starting with system (3) the final products; if we suppose the changes to be reversed, that is, the heat to be reapplied in inverse order to that in which it was lost, it is evident that we would reproduce (2), the initial state of combination of the products, and find them largely dissociated.

We have now reduced the question to this. Certain gaseous products (see equation of metamorphosis above) confined at constant volume, are subjected to a potential heat of 348,354 units. What will be the dissociation?

The detonation of a confined solid or liquid explosive (case 1) is analogous to the formation of a gas, by the detonation of its components at constant volume (case 2), with this difference: in case (1) the potential heat and gas-forming power are concentrated in the solid or liquid body, whereas in the gas we start with its components in the gaseous state, and the heat developed is its potential heat of formation. However, in determining the initial state of combination of the products, we proceed practically in the same way in the two cases. We work backwards from the final products by applying heat to them, and ascertaining as well as we can the resulting dissociation. In the case of the gaseous mixture, the heat applied is the potential heat of formation of the gas. In case (1) the heat is not that of formation of the products, but H—the heat of metamorphosis of the explosive.

Estimates of Dissociation in Products of N.G.—We can get an approximate value for the amount of dissociation by assuming that it is confined to the triatomic gases, and that these are split into their diatomic components. Dissociation assumed to be confined to triatomic molecules.

In the heats of formation, or latent heats of dissociation, we have

CO_2 split into $\text{CO} + \frac{1}{2} \text{O}_2 \quad 3 \times 67,670 = 203,010$

H_2O split into $\text{H}_2 + \frac{1}{2} \text{O}_2 \quad 2\frac{1}{2} \times 57,632 = 144,080$

The total heat applied—348,354 units, being divided among 5.5 triatomic molecules, and 1.75 diatomic (equal to 1.167 triatomic)—total 6.667 triatomic, the heat applied to

H
each triatomic molecule is $52,253$ units $= \frac{\text{---}}{6.667}$.

Using this in our general formula for triatomic dissociation,
 $.59 \text{ Nh}$

$n^{111} = \frac{\text{---}}{Q}$, we have

$$\text{For } \text{CO}_2, n^{111} = \frac{.59 \times 3 \times 52.253}{67,670} = 1.367.$$

$$\text{For } \text{H}_2\text{O}, n^{111} = \frac{.59 \times 2\frac{1}{2} \times 52.253}{57,632} = 1.337.$$

Total 2.704, or 49.45 per cent. of the triatomic molecules are dissociated.

For the heat rendered latent we have:

$$1.367 \times 67,670 = 92,488$$

$$1.337 \times 57,632 = 77,056$$

$$\underline{\hspace{10em}} = 169,544 = 48.67 \text{ per cent of H.}$$

The active heat is 51.33 per cent. of H, or 178,810 units.

The specific heat is not changed.

$$\frac{178,810}{48.44} = 3691.4^\circ = t.$$

$$3691.4^\circ + 273 = 3964.4^\circ = T.$$

$$3964.4^\circ$$

$$\frac{\text{---}}{273} = 14.52 \text{ atmospheres — pressure at spec. vol.}$$

The specific volume has been increased in the proportion 14.50 to 17.204 (twice the number of molecules in the dissociated system), and is 13.555 cubic feet instead of 11.423 cubic feet.

The pressure, 14.52 atmospheres, corresponds to a density
1

844.21

At unit density the pressure is $14.52 \times 844.21 = 12,259$ atmospheres.

At absolute density of N.G. (1.60) = 19,615 atmospheres.

The temperatures are 51.33 per cent. of the theoretical.

The pressures are 62.56 per cent. of the theoretical.

Dissociation of both Triatomic and Diatomic Molecules.—

This case is complicated, because we have to consider the two triatomic gases separately, also CO separately from the other diatomic gases.

Let $n^{111} c$ = number CO_2 molecules dissociated into CO and O_2

$n^{111} h$ = number H_2O molecules dissociated into H_2 and O_2

$n^{11} c$ = number CO molecules dissociated into C_2 and O_2

n^{11} = number other diatomic molecules dissociated

$m^{111} c$ = number integral CO_2 molecules in dissociated system

$m^{111} h$ = number integral H_2O molecules in dissociated system

$m^{11} c$ = number integral CO molecules in dissociated system

m^{11} = number other diatomic molecules in dissociated system

m^1 = number monatomic molecules in dissociated system

heat units

Let Q_c = heat of formation of CO_2 from CO and $\text{O} =$ 67,670

$Q^1 c = Q_c =$ heat of formation of CO from C_2 and O_2 (Thomsen's hypothesis) 67,670

Q_h = heat of formation of H_2O from H_2 and $\frac{1}{2} \text{O}_2$ 57,632

Q^1 = heat of formation of diatomic molecules (except CO) 38,421

H = potential heat applied 348,354

$$\text{Appealing to our general formulas } n^{111} = \frac{.59 \text{ Nh}}{Q}, n^{11} = \frac{0.385 \text{ N}^1 h^1}{Q^1}$$

We have for the triatomic molecules—the number to be considered, 5.5 plus the equivalent of the diatomic ($\frac{2}{3} 1.75$) = total 6.666 = N.

The average heat applied to each is therefore $h = H - n^{11}c Q_c - n^{11} Q^1$.

$$\text{We have for CO}_2, n^{111}c = .59 \times 3 - \frac{(H - n^{11}c Q_c - n^{11} Q^1)}{6.666 Q_c} \quad (a)$$

$$\text{For H}_2\text{O, } n^{111}h = \frac{.59 \times 2\frac{1}{2} (H - n^{11}c Q_c - n^{11} Q^1)}{6.666 Qh} \quad (b)$$

For CO the number of molecules sharing the heat is 10—

$$N^1 = 3 - m^{111}c h = \frac{m^{111}c Q_c + m^{111}h Qh}{10}$$

For the other diatomic molecules, $n^1 = 7 - \frac{1}{2}m^{111}c - 1\frac{1}{2}m^{111}h$,

$$h = \frac{m^{111}c Q_c + m^{111}h Qh}{10}$$

Therefore,

$$n^{11}c = \frac{.385 (3 - m^{111}c) (m^{111}c Q_c + m^{111}h Qh)}{10 Q^1 c} \quad (c)$$

$$n^{11} = \frac{.385 (7 - \frac{1}{2}m^{111}c - 1\frac{1}{2}m^{111}h) (m^{111}c Q_c + m^{111}h Qh)}{10 Q^1} \quad (d)$$

HIGH EXPLOSIVES.

By solving equations (a), (b), (c) and (d) we find for the dissociation and heat rendered latent as follows:

$$\text{CO}_2 \text{ } n^{111}c = 1.208 \times 67,670 = 81745.4$$

$$\text{H}_2\text{O} \text{ } n^{111}h = 1.2346 \times 57,632 = 71152.5$$

$$\text{CO} \text{ } n^{11}c = 0.1334 \times 67,670 = 9027.2$$

other diatomic mol.—

$$n^{11} = 0.8184 \times 38,421 = 31443.7$$

193,368.8 heat units

The active heat = 348,354 — 193,368.8 = 154,985.2
heat units.

The active heat is 44.49 per cent. of H.

The latent heat is 54.51 per cent. of H.

The dissociated system from which we calculate the specific heat and volume is as follows:

		atomic heats
CO ₂	m ¹¹¹ c	1.7920 × 3 5.3760
H ₂ O	m ¹¹¹ h	1.2654 × 3 3.7962
CO	m ¹¹ c	1.0746 × 2 2.1492
other diatomic mol.	m ¹¹	3.5209 × 2 7.0418
monatomic mol.	m ¹	1.6368 × 1.23 2.0133
Total no. mol.		<u>20.3765 × 2.422</u>
= 49.352	Kv spec. heat.	

$$\text{Specific volume} = 2 \times 9.2897 = 18.5794.$$

$$\frac{154,985.2}{49.352} = t = 3140.4^\circ \text{ rise of temperature, 43.7 per cent. of}$$

the potential value.

$$3140.4 + 273 = 3413.4^\circ = T \text{ absolute temp.}$$

3413.4

$$\frac{273}{3413.4} = 12.5033 \text{ atmospheres pressure at spec. volume.}$$

$$\frac{18.5794}{14.50} = 12.5033 \times \frac{18.5794}{14.50} = 16.021 \text{ atmospheres.}$$

The specific volume of the system being 18.579, as against 14.50 for the final products, the pressure at specific volume of

1

This is at a diversity of $\frac{1}{713.07}$. At unit density it will
be $16.021 \times 713.07 = 11,424$ atms.

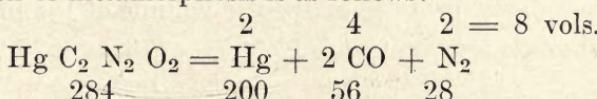
At the absolute density of nitro-glycerine (1.6) it is 18,278 atmospheres.

The potential absolute pressure being 31,195, this is 55.39 per cent. of the potential.

Herr Bichel calculated the absolute pressure of blasting gelatin (which closely approximates nitro-glycerine in regard to heat and energy) from the observed pressure at a density of $\frac{1}{150}$, and obtained 16,658 atmospheres (see footnote, page 121, chapter X., where it is shown that this is 52.5 per cent. of the potential pressure for blasting gelatin). The result for the absolute pressure of nitro-glycerine given above, 18,278 atmospheres, shows a fair agreement with this, but is probably somewhat too high, because of our treatment of carbon in the volatile state as a perfect gas. If we deduct about 4 or 5 per cent. as a guess, and call the absolute pressure of nitro-glycerine 17,500 atmospheres, we shall not be far wrong.

The temperature attained, 3140° C., agrees very fairly with Herr Bichel's estimate, 3216° C. for blasting gelatin, using the French empirical formulas to attain the specific heat.

Mercury Fulminate.—This explosive being an endotherm, the dissociation of its products is specially interesting. The equation of metamorphosis is as follows:



$$\begin{aligned} 284 \text{ French Criths} &= 25.44 \text{ grammes, give } 8 \text{ litres gas.} \\ &\quad 1000 \text{ grammes give } 314.46 \text{ litres gas.} \\ 284 \text{ British Criths} &= 1.58813 \text{ pounds give } 8 \text{ cubic feet} \\ &\quad 1 \text{ pound gives } 5.0375 \text{ cubic feet} \\ &\quad = v \text{ specific volume.} \end{aligned}$$

The heat of metamorphosis as determined by Berthelot and Vieille is 116,000 heat units (this includes the heat of condensation of the mercury vapour).

We have, therefore,

$$2 \text{ CO} \times 29,290 = \quad \quad \quad 58,580$$

$$\text{Deduct heat of formation of the ful-} \\ \text{minate (added since it is negative)} \quad \underline{-57,420}$$

116,000 heat units

Since we take the mercury as gaseous, we must deduct the latent heat of volatilisation of 200 units of mercury vapour (*15,400 heat units) which leaves:

$$\text{H—heat for 284 units, or one molumass of} \\ \text{fulminate} =$$

100,600

$$\text{heat for 1 unit or one molumass of} \\ \text{fulminate} =$$

354,225 heat units

Specific heat:

$$4 \text{ vols. CO} = 4$$

$$2 \text{ vols. N}_2 = 2$$

$$2 \text{ vols. Hg} = 1.23$$

$$\frac{7.23 \times 2.422 = 17.511 = K_v, \text{ the total spec. heat}}{100,600}$$

$$\frac{17.511}{5744.9} = 5744.9^\circ = t \text{ rise in temperature.}$$

$$\frac{5744.9}{273} = 21.043 \text{ atmospheres increase of pressure.}$$

Add one atmosphere and we have

22.043 atmospheres pressure at specific volume of the product.

The absolute temperature is $5744.9 + 273 = 6017.9 = T.$

The pressure given is at a density of $\frac{1}{314.46}.$

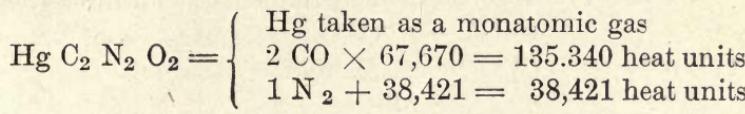
The pressure at unit density therefore = 6931.77 atmospheres.

At the absolute density of mercury fulminate (4.416) = 30,611 atmospheres potential value.

*This also includes the heat of the liquid mercury between the boiling point and 0° C.

Dissociation of Products of Mercury Fulminate.—We first consider the heat relations of the metamorphosis giving the final products shown above. Mercury fulminate, like all other chemical compounds, according to our view, has a positive heat of formation.

We can bring out this fact by writing the thermal reaction as follows:



$$\text{Deduct heat of formation of fulminate } 73,161 \text{ heat units}$$

$$\text{H} = 100,600 \text{ heat units}$$

That is, the heat of formation of the fulminate from mercury, monatomic nitrogen and diatomic oxygen, and gaseous carbon, is 73,161 units. If the gaseous carbon and oxygen are taken as monatomic, this heat value will be still higher. If we take the fulminate as formed from solid amorphous carbon and diatomic nitrogen and oxygen, and assume that these molecules have no heats of formation, the value becomes—57,420, as given in the first calculation.

In computing the dissociation, we apply the general formula:

$$n^{11} = \frac{.385 \text{ Nh}}{Q}$$

to all the diatomic molecules CO and N₂, as well as the C₂ and O₂ resulting from the splitting of the CO.

Let n^{11c} = no. molecules of CO dissociated.

N¹¹ = no. molecules of N₂ dissociated.

n¹¹ = no. molecules of C₂ and O₂ dissociated.

The heat equivalent of the diatomic molecules is 4.23—mercury being monatomic is taken as 1.23.

Referring to the general formula, we have

$$H - n^{11} Q^1$$

$$\text{for CO} \quad N = 2 \quad h = \frac{1.23}{4.23}$$

$$\text{for } N_2 \quad N = 1 \quad h = \frac{H - n^{11}c Q_c - n^{11} Q^1}{4.23}$$

$$\text{for } C_2 \text{ & } O_2 \quad N = n^{11}c \quad h = \frac{H - n^{11}c Q_c - N^{11} Q^1}{4.23}$$

These values substituted in the general formula give:

$$(1) \quad n^{11}c = .770 \frac{(H - n^{11} Q^1)}{4.23 \quad Q_c}$$

$$(2) \quad N^{11} = .385 \frac{(H - n^{11}c Q_c - n^{11} Q^1)}{4.23 \quad Q^1}$$

$$(3) \quad n^{11} = .385 \frac{n^{11}c}{4.23 \quad Q^1}$$

From which we obtain the following dissociation values:

$$\begin{aligned} \text{For CO} \quad - n^{11}c &= .1255 \\ N_2 \quad - N^{11} &= .0904 \\ C_2 \text{ and } O_2 \quad - n^{11} &= .1404 \end{aligned}$$

The value of n^{11} shows that there is some error in our hypothesis as to the heats of formation, since the number of C_2 and O_2 molecules dissociated cannot exceed $n^{11}c$, the number set free by the splitting of the CO. A similar anomaly was noticed in calculating the dissociation for the detonating gaseous mixture $CO + O$ (see chapter XI.), for which we used the same values for the heats. We there remarked that it could be accounted for by either too great a value for the heat of formation of CO, or too small a value for that of C_2 and O_2 . In the present case it is evidently to be explained by too small a value for the latter (38,421), and as we have tested the value for O_2 , and found it approximately correct, we are justified in believing that the heat of C_2 from monatomic C is larger than 38,421—if, in fact, our hypothesis as to the volatilisation of carbon and its temporary existence as a diatomic gas be correct. This hypothesis involves no error in itself, provided we get proper values for the heats concerned. Another, and more general, explanation, would be that we have used too small a

specific heat for the carbon. This is probably abnormally large, which would increase the divisor in the value for n^{11} in equation (3).

Since there is only a small difference between the values found for $n^{11}c$ and n^{11} , we take them equal.

The heat rendered latent is as follows:

$$n^{11}c = .1255 \times 67670 = 8492.6$$

$$N^{11} = .0904 \times 38421 = 3473.3$$

$$n^{11} = .1255 \times 38421 = 4821.8$$

$$16,787.7 = 16.69 \text{ per cent. of H.}$$

The active heat is $100,600 - 16,787.7 = 83,812.3$ heat units.

The dissociated system is as follows:

	No. molecules.	Atoms.	Atomic heat.
CO	1.8745	3.7490	3.7490
N ₂	.9096	1.8192	1.8192
C, O, & Hg	1.4318	1.4318 × 1.23	1.7611
	4.2159	7.000	$7.3293 \times 24.22 = 17.7516$ spec. heat Kv.

Specific volume, $2 \times 4.2159 = 8.4318$.

From these data we obtain:

t rise in temperature, $4721.5^\circ \text{ C.} = 82.2$ per cent. of the potential value.

T absolute temperature, 4994.5.

P¹—pressure at specific volume of the dissociated system 18,295 atmospheres.

pressure at specific volume of the final products (8.4318p)

8

= 19.28 atmospheres.

This is at a density of $\frac{1}{314.46}$. The pressure at unit density is therefore 6063.6 atms.

At the absolute density of mercury fulminate (4.416) it will be 26,777 atms.

We calculated the potential value of the absolute pressure to be 30,611 atms.

This shows a decrease on account of dissociation of about 12 per cent. Our guess, in chapter IV., of 10 per cent., was therefore too low.

By comparing this calculation with those for detonating gaseous mixtures, we are led to believe that we have somewhat underestimated the effect of dissociation on the products of mercury fulminate, both in regard to temperature and pressure. While the study is a theoretical one we can draw certain safe conclusions from it.

The temperature reached, and the pressure exerted by the products of mercury fulminate at absolute density of charge, notwithstanding its small relative energy, are the highest of any known explosive. It owes this to two things—its great density and the relatively small effect of dissociation—as was first pointed out by Berthelot, who, however, believed that dissociation was entirely absent.

We can also safely conclude that the temperature reached by the products of explosives is something less than 4700° C. We found for nitro-glycerine 3140°. That for blasting gelatin will be a little greater. The potential heat will be a little higher, there being nearly 80 per cent., instead of 76 per cent., of triatomic gases, but the dissociation will also be somewhat greater. Of industrial explosives, blasting gelatin reaches probably the highest temperatures, but even this is 1200° to 1500° below that of mercury fulminate.

Question of Specific Heats.

The relation between the specific heats and the laws of trical substance, showing equal increments of temperature for equal increments of heat. There are two ways in which a gas can be made to indicate temperature, viz., (1) by increase of pressure at constant volume, or (2) by increase of volume under constant pressure. In a perfect gas the increment of pressure gases is simple. A perfect gas is simply a perfect thermome-

bears to the increment of temperature (case 1) a constant relation, which is the same as the relation which the increment of volume bears to the increment of temperature (case 2), and in each case equal increments of temperature correspond to equal increments of heat. For every gas, when treated in the first way, the increment of heat per degree of temperature is the specific heat at constant volume, and when treated in the second way this increment (which includes the external work done against the constant pressure) is the specific heat under constant pressure. To fulfil the conditions of a perfect gas these elements must remain constant.

The law of Boyle is simply expressed by $pv = \text{constant}$. This supposes the temperature to remain constant. A more complete expression, which includes the law of Charles, is:

$pv = RT$, in which R is the co-efficient of expansion or tension, and T is the absolute temperature. The relation between the co-efficient and the specific heats is:

$$R = J (K_p - K_v),$$

that is, the co-efficient is the mechanical equivalent of the difference between the specific heats at constant pressure and constant volume. From which we have the fundamental equation,

$$Pv = J (K_p - K_v) T,$$

in which p, v, K_p and K_v relate to the volume of unit mass of the gas.

A gas undergoes an adiabatic change when it expands or is compressed without loss or gain of heat as such. The law for the change is expressed by

$$K_p$$

$Pv^y = \text{constant}$, in which $y = \frac{K_p}{K_v}$, the ratio of the specific heats.

When the gas is compressed, the work of compression is transformed into heat, and the volume is less for the same pressure than in an isothermal change. When it expands it does work, and this is a tax upon its heat, so that the volume is again less than for the isothermal change of pressure. The adiabatic

curve is therefore steeper than the isothermal. The greater the $\frac{K_p}{K_v}$ value of — the steeper the adiabatic, and the greater the efficiency of the gas in converting heat into work.

These relations are clearly brought out in the Kinetic theory of gases, which is simply an hypothesis to explain the behaviour of gases. For instance, when we compare equal volumes of two gases, one diatomic and the other triatomic, we find that more heat is required to raise the temperature of the latter a given number of degrees, although the co-efficients of expansion or extension are equal—that is, $K_p — K_v$ is the same for the two gases. The Kinetic theory explains this, by supposing the more complex gas to absorb more heat internally—heat which consists of motions of the parts of the molecules, and does not contribute to the Kinetic energy of the gas. Ac-

cording to the same theory, the ratio $\frac{K_p}{K_v}$ depends upon the mole-

cular constitution of the gas—the maximum being $1\frac{1}{3}$ for monatomic gases—the possible minimum towards which very complex gases tend is 1. The value of the ratio for diatomic gases is about 1.41, for triatomic, 1.27, etc.

Specific Heats not increased at Explosion Temperatures.—While there may be a question as to the exactness of the values 1.41, 1.27, etc., since there are no perfect gases in nature by which to check them experimentally, there can be no doubt as to their approximate correctness, and also as to the general prin-

ciple that the ratio $\frac{K_p}{K_v}$ diminishes with the complexity of con-

stitution of the gas. All authorities agree that $K_p — K_v$ equal constant is a working hypothesis for all gases. It is universally employed in the study of explosives, and, like Avogadro's law, the foundation of the chemistry of gases, it receives the assent, tacit, or acknowledged, of all students and investigators. Now, one of the strongest arguments which can be brought against the theory sometimes applied to explosives, viz., that the specific

heats of a gas increase with the temperature is this: *If two quantities that have a constant difference between them increase with the temperature, the ratio between them becomes less—which means that the constitution of the gas becomes more complex at higher temperatures—an effect which is contrary to the known effects of heat.*

Boyle's Law at High Densities.

One of the questions which have been subjects of controversy among the authorities on explosives, is this: Does Boyle's law, pv constant, hold good under great densities of charge? The question is independent of another, which we have already considered, and would better be put in this form. Assuming that the gases of an explosive exert a true pressure, and not a dynamic effect, does Boyle's law, pv constant, hold good under great densities of charge?

The question cannot be answered off-hand, but we can throw some light on the subject.

Physicists divide gases into permanent gases and vapours. Permanent gases are those which cannot be liquefied by pressure. With rise of temperature all gases and vapours (which are not decomposed by the heating) become permanent. Above its absolute boiling point a gas cannot be liquefied. Thus at about 31° C., carbon dioxide becomes a permanent gas. At high temperatures, therefore, there is no such distinction to be made.

A perfect gas is one which obeys the laws accurately—that is, it has a constant co-efficient of expansion, which is equal to the constant co-efficient of tension. While none of the known gases is perfect, some are much nearer the ideal in their behaviour at ordinary temperatures than others. If we arrange a table of gases in the order of their critical temperatures, or absolute boiling points, we get a very accurate classification of gases according to their "degrees of perfection," when tested at ordinary temperatures. The following is a short table on the authority of Professor Olszewski, of the University of Cracow (see "Chemical News" of February 1st, 1895). The absolute

boiling point, or critical temperature (t.c.) is given in centigrade degrees; the critical pressure (p.c.), that is, the pressure necessary to produce liquefaction at the critical temperature, is given in atmospheres.

Table of Permanent Gases.

Symbol.	Molecular mass.	t.c.	p.c.
Hydrogen, H ₂	2 ..	—220° ..	20
Nitrogen, N ₂	28 ..	—146° ..	35
Carbonic Oxide, CO	28 ..	—139.5° ..	35.5
Argon, A	38 ..	—121° ..	50.6
Oxygen, O ₂	32 ..	—118.8° ..	50.8
Nitric Oxide, N.O	30 ..	—93.5° ..	71.2
Methane, CH ₄	16 ..	—81.8° ..	54.9

Though the “degree of perfection” of a gas bears a general relation to the simplicity of its constitution, and the smallness of its molecular mass, a glance at the table shows that its behaviour cannot be explained by an appeal to these things. It is simply a question of removal from the critical temperature. We therefore draw the conclusion that a gas progressively approaches the ideal state as its temperature is raised above the critical point. Maxwell says (see page 179, “Theory of Heat”), “It is probable that when the volume and the temperature are sufficiently great, all gases fulfil with great accuracy the gaseous laws.”

Isothermals of a Perfect Gas.—Our next step will be a brief study of the behaviour of a perfect gas, and for this purpose we make a diagram, Fig. 7, of some of the isothermals arranged according to the absolute scale of temperature. The ordinates represent pressures, and the abscissas volumes. The law of Boyle—Pv constant, is embodied in each of these isothermals. Let us consider the lower one, marked 273°, corresponding to the ordinary temperature 0° C.

From the equation Pv = c these isothermals are rectangular hyperbolæ, the axes OA and OB being asymptotes. For the point P, let the pressure and the volume — PQ and PR be each equal to unity. Then, for any other point, as P', pv = 1. If

at any point, as P, we draw a tangent PF to the curve, then from the properties of the hyperbola, the subtangent on the asymptote $FR = RO = PQ$, the ordinate of the point P. FR represents the elasticity of the gas (see Maxwell's "Theory of Heat," page 108), and we see that so long as the temperature is kept constant this is equal to the pressure.

These properties pertain to each of the isothermals. The law of Charles combined with that of Boyle ($pv = RT$), enables us to pass from one to the other; that is, knowing the pressure

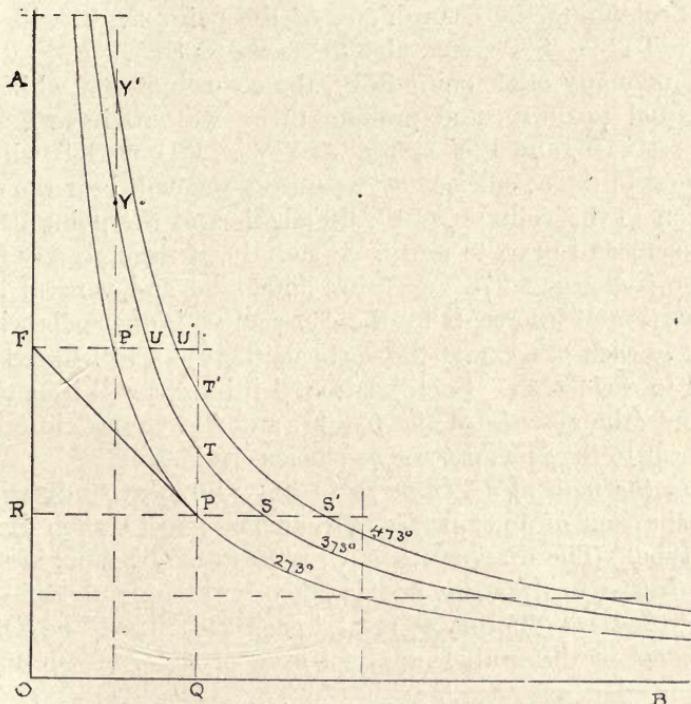


Fig. 7.—Isotherms of a Perfect Gas.

corresponding to a certain volume (or vice versa), for one of the isothermals, this complete expression for the law, enables us to predict it for any other isothermal. In this sense the product pv is not a constant, but is proportional to the absolute temperature.

If the isothermals be drawn for consecutive degrees of temperature, then, for the point P, for which the co-ordinates are each equal to unity, PT and PS are the co-efficient of tension and co-efficient of expansion, respectively. These are equal, and may be taken as approximately equal to $\frac{1}{273}^*$, or 0.00367. This is independent of the properties of any particular gas, being based on the laws of Thermodynamics and the scale of temperature. For convenience, we have drawn the isothermals of consecutive 100 degrees, and PT and PS will be each equal to 0.367.

Prolonging the co-ordinates of the point P, we will have $PT = TT' = T'T''$, etc., also $PS = SS' = S'S''$, etc., = 0.367. If we take any other point as P', the co-ordinates of which are not equal to unity, and prolong them, we will have $P'U = UU' = U'U''$, and $P'Y = YY' = Y'Y''$. $P'U$ or UU' will not be equal to the co-efficient of expansion, but will bear the same relation to the volume (FP' , the abscissa of the point P'), as the co-efficient bears to unity. Generally, if through any point on the isothermal 273° we draw horizontal and vertical lines, the horizontal intercepts by the consecutive isothermals will be equal to each other, and the vertical intercepts will likewise be equal to each other. Each horizontal intercept will bear to the volume (the abscissa of the point), and the vertical intercepts will bear to the pressure, the co-efficient ratio.

Isothermals of an Imperfect Gas.—Our next study will be the behaviour of an imperfect gas, and we select carbon dioxide as a type. The diagram, Fig. 8, represents Dr. Andrew's experiments upon this gas, and is taken with slight modification from Maxwell's "Theory of Heat," page 120. It will be noticed that none of the isothermals, not even of those for air in the

*According to Sir William Thompson's latest calculations, based on the noted experiments made by him in conjunction with Dr. Joule (see article, Heat in Encyclop., Brit., 9th edition), this ratio may be taken as

1

— —that is, if the interval between the freezing and boiling points of 273.1

water under atmospheric pressure be taken as 100 degrees, the true temperature of melting ice may be taken at 273.1° above the zero of the absolute scale.

upper right hand corner, is symmetrical with reference to the axis, but this is easily explained. The base line of the diagram is taken at 47 atmospheres instead of zero pressure. The

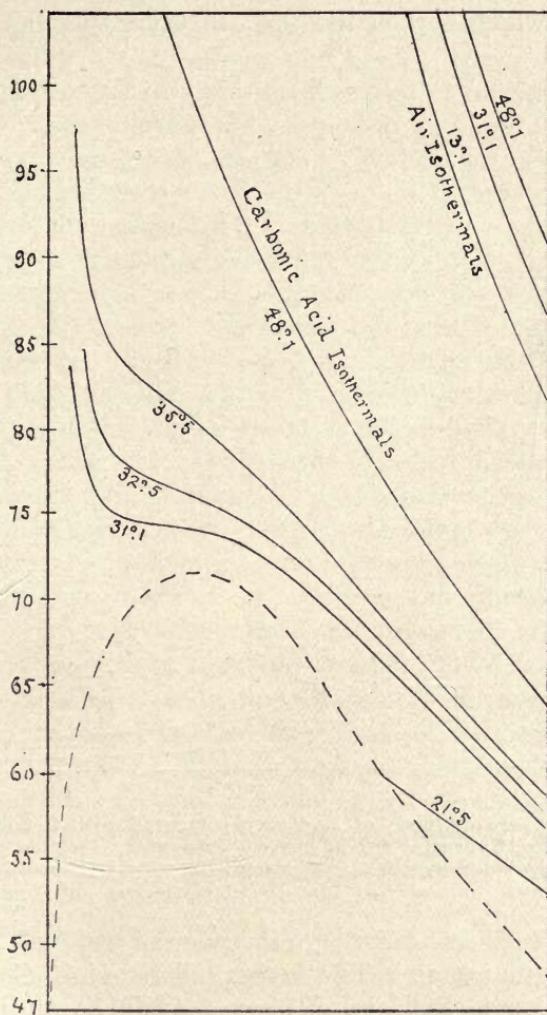


Fig. 8.—Isotherms of Carbonic Acid.

diagram, in fact, is a small piece cut out of the general map of the isotherms, the piece being purposely taken in that part

of the field which is near the critical point. The isothermals are numbered according to the centigrade scale, but are not consecutive. The critical temperature is 30.92° , the critical pressure about 73 atmospheres. The dotted line encloses the region in which carbon dioxide can exist as a liquid in the

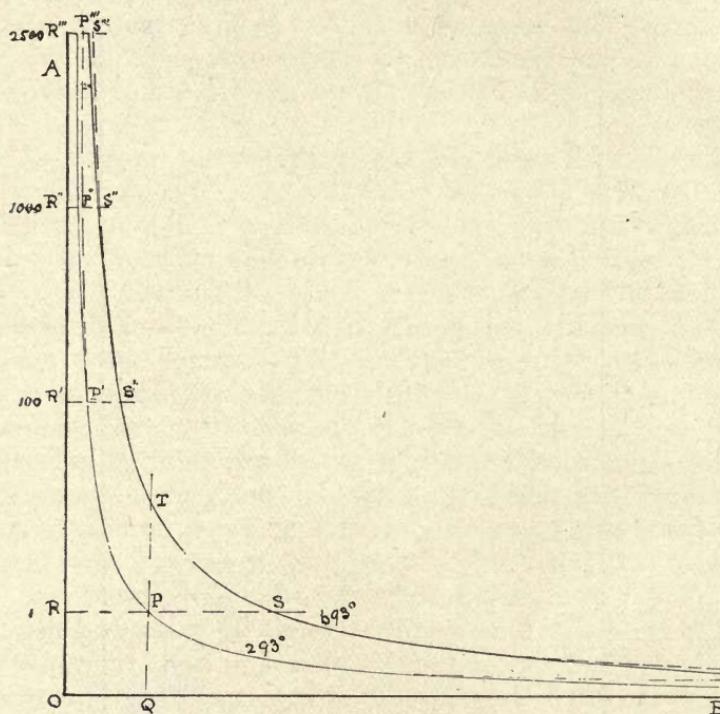


Fig. 9.—Isotherms of Hydrogen compared with the ideal.
Isotherms for Hydrogen are in broken lines where they do not coincide with the Hyperbolæ, which are represented by full lines. The diagram cannot be drawn to scale, so that the deviation is only indicated in a general way.

presence of its vapour. The isothermal for 48.1° C. shows an approximation to the laws of gases. At this temperature, to quote Maxwell, carbon dioxide "has all the properties of a gas, and the effects of heat and pressure on it differ from their effects on a perfect gas only by quantities requiring careful experiments to detect them."

We note that careful experiments do detect them, and if the diagram were sufficiently extended the deviation of the isothermal from a true hyperbola could be seen by the eye.

The diagram is intended, however, to show the irregularity in the isothermals near the critical point. *A similar irregularity is to be found in the isothermals of every gas near its critical point.* The irregularity may be described as follows: *the gas is much more compressible than required by Boyle's law.*

As the isothermals are taken further and further away from the critical temperature, the curves become more nearly normal, but the irregularity is transmitted in a modified form many degrees from this particular isothermal. The propagation and gradual extinction of the irregularity may be likened to the rings in the cross section of a tree, which has a deformed heart or centre. The presence of this irregularity in many gases is only detected by very delicate experiments. The co-efficient of expansion or tension is not absolutely constant for any gas, but when the co-efficient is found to increase, and then as the pressure rises it decreases, it indicates this sort of irregularity in the isothermals. If, in compressing a gas at constant temperature, the product pv is less than the normal, and afterwards, at higher pressures, pv approaches the normal, then the isothermal for that temperature has preserved a trace of the irregularity prevailing near the critical temperature.

This has been made the subject of an investigation by Mendelieff, based upon the experiments of Regnault and Natterer, as confirmed by Amagat. *All gases except one show this deviation.* The only gas in which this irregularity cannot be detected is hydrogen, and this is the one in which the temperature of the experiment is furthest removed from its critical temperature.

Now, have we any positive proof that an ordinary gas, such as air, tends to correct its behaviour as the temperature rises? Mendelieff found (see page 133, Prin. Chem., vol. 1) that for gases which are more compressible than required by Boyle's law (this applies to all gases at ordinary pressures except hydrogen) the *co-efficient of expansion increases with the temperature.*

This does not apply, as we shall see presently, to the extremes of the curves, but especially to that portion where the irregularity is noticeable. In this region, since the gas is more compressed than it should be, its isothermal curve lies inside (to the left) of the true hyperbola. For any point on the isothermal, the horizontal distance to the next consecutive (1° difference) isothermal divided by the abscissa of the point, will be the co-efficient of expansion. Taking a number of isothermals, it is evident that if the ratio of these distances increases, the curves will become more nearly normal for higher isothermals.

We therefore draw this conclusion: *All gases at temperatures sufficiently removed from their critical temperatures will at least reach the perfection shown by hydrogen at ordinary temperatures.*

Isothermals of Hydrogen.—The most perfect of the gases at ordinary temperatures, hydrogen, shows a decided departure from Boyle's law at both extremes, that is, under great condensation and rarefaction, and the departure is even more decided in the case of the other permanent gases. We make a brief study of this interesting gas hydrogen, basing our study upon the experiments of Amagat, and using the diagram of isothermals (Fig. 9) to illustrate them. Amagat's compressions were made at 20° C., corresponding to the isothermal 293° . The diagram cannot be drawn to scale, but the deviation of hydrogen from Boyle's law is roughly indicated on it. For the point P, let p and v each be equal to unity—p being equal to one meter of mercury pressure, and v equal to one litre. Let the ordinate of P' represent a pressure of 100 meters of mercury—then the corresponding volume R'P' to fulfil the law should be $\frac{1}{100}$ of a litre. Instead of this, it was found to be 0.0107, or 7 per cent. too large. At P'', the pressure being 1000 meters of mercury, the volume R''P'' should have been $\frac{1}{1000}$. It was really 0.0019, or nearly double the normal. At P'''—pressure 2500 meters of mercury (about 3290 atmospheres), the volume should have been 0.0004; it was found to be 0.0013, or three times the normal.

To sum up the properties of hydrogen, its behaviour at medium pressures is almost identical with that of a perfect gas, but at great pressures the volume is too large—that is, the branch of its isothermal in the direction of A does not approach the asymptote rapidly enough. In regard to the other branch towards B, a similar (and probably exactly equal) deviation from the normal is shown to exist by Mendelieff. He found that hydrogen, like air, and all gases, is less compressed at *low pressures* than required by Boyle's law—that is, for a given attenuated volume the pressure is greater than the normal. This makes it quite certain that the isothermal is a symmetrical curve. This symmetrical hydrogen curve seems to be “a stage of perfection” towards which all gases tend as they are further and further removed from their critical points. That is, the irregularity we mentioned above gradually disappears, and they obey, like hydrogen, the laws of gases in the middle register (as we may term it), and depart from these laws under either great condensation or rarefaction. Now, are we at liberty to believe that by a still further removal from the critical point we may get a still closer approximation to the ideal hyperbolic curve than is given by even this typical hydrogen isothermal?

The obstacle to the *unconditional* fulfilment of Boyle's law is insuperable. The resistance offered by hydrogen and all other gases to extreme condensation lies in the nature of matter. There must be a limit to the density—approached by degrees—beyond which the gas ceases to yield to pressure. To illustrate, let us take a cubic foot of hydrogen, which, at 0° C., under one atmosphere of pressure, weighs 0.0056 pounds. Let us subject this cubic foot of gas to a pressure of 10,000 atmospheres, keeping the temperature constant. If Boyle's law held good, the resulting volume would be $\frac{1}{10,000}$ of a cubic foot, and the hydrogen would have $\frac{1}{10}$ the density of water, or a density 9 times as great as the probable limit— $\frac{1}{10}$, according to Mendelieff.

Let us now try the effect of raising the temperature of the experiment. If we take the cubic foot of hydrogen at a very high temperature, say 5460° C., then the cubic foot would weigh only 0.00028 pounds, and increasing the pressure to

10,000 atmospheres, gives, according to Boyle's law, a density of only 0.045, which is not impossible, seeing that it is less than two-thirds of that actually reached in Amagat's experiments with less than one-third of the pressure.

Improvement with Temperature.—This argument *proves* nothing, but the question being one of degree, it removes a difficulty in extending the laws of gases to greater pressures. The obstacle is mainly the crowding of the molecules. At high temperatures we reach a given great pressure with less crowding. The argument shows that the laws of gases have a better chance to apply when the temperature is increased, but it does not show that they do apply. However, we have better evidence than this. Again we appeal to Mendelieff. His investigations with Kayandu (1870) showed that for gases which are less compressible than required by Boyle's law (this is the case with *all* gases under great pressures), the expansion by heat decreases with increase of pressure. Since the volume is already too great, this tends to bring it to the normal. The fact that all gases at great pressures are less compressible than indicated by $pv = \text{constant}$, is proved by the researches of Natterer, Cailletet and Armagat—that is, for all gases the irregularity in their behaviour passes into the normal deviation at great pressures, and then the co-efficient of expansion decreases with increase of pressure.

The practical determination of the co-efficient implies the drawing of at least two of the isothermals. In Mendelieff's experiments, the first is at $0^{\circ}\text{C}.$, or 273° absolute (this we may take as approximately represented in the diagram by Amagat's -293°), the second at an interval of 100 degrees— 373° .* For a point such a P' , on the first isothermal, the co-efficient (for 100° interval) is the ratio of the horizontal distance between the two isothermals to the corresponding volume or abscissa of the point. As the ratio of these distances was found to decrease, it is evident that the second isothermal is nearer the ideal than the first—that is, the coincidence of the curve with the hyperbola is carried to greater pressures for higher isothermals.

*For greater clearness we have taken in the diagram an interval of 400 degrees between the two isothermals.

The conclusion is that the symmetrical isothermal of hydrogen at ordinary temperatures is not a limit to the "degree of perfection" of gases, but that this curve, towards which they all tend at elevated temperatures, is subject to further change, approximating more and more closely to the ideal as the temperature rises.

Pv Increased at Great Densities.—We first showed that all gases when sufficiently removed from their critical points attain the hydrogen standard, and obey the laws of gases with great accuracy, except in the regions of extreme pressure and attenuated volume.† We now see that as the temperature continues to increase the laws can be extended further and further into these regions, and we conclude that these laws can be extended well towards the states of high temperatures and great compressions characteristic of explosives—provided that the first condition of these laws, viz., equilibrium, obtains.

This is not to say that Boyle's law holds rigidly under the enormous compressions in closed vessels pertaining to densities of charge equal to and greater than unity—even at explosion temperatures. The discrepancy will certainly be smaller than for the same compressions at lower temperatures, but it seems philosophical to expect a positive deviation increasing with the density—that is, pv will be larger than the normal, and v being fixed by the volume of the confining vessel, p will have a greater value than called for by Boyle's law.

However, if the variation of the pressure with the density of charge is ever worked out and formulated, it is certain that it will prove to be governed by a true law, showing a regulated increase of the pressure with increase of density, and we are justified in rejecting the hypothesis of Berthelot (see page 28, "Explosives and Their Power"), viz., that Boyle's law does not hold good for medium densities, but is re-established at high densities—an hypothesis based upon an erroneous interpretation of crusher gauge readings.

†There is a similar improvement in the region of rarefaction, but it is not necessary to our purpose to follow it.

Experimental Evidence.—In this case we can appeal to actual experiment to support our views. Nobel and Abel, in their elaborate researches, applied Boyle's law to the gaseous products of gunpowder, making allowance for the volume taken up by the solid products (liquid at the temperature of the explosion), and obtained a table of pressures for the different densities of charge which closely approximate the pressures obtained in their practical experiments. This serves to show that Boyle's law holds good at least approximately for pressures up to 6000 atmospheres. But the presence of the solid products is a complication of best which weakens the argument.

Fortunately, there is better evidence than this. In later years, Captain Nobel (then Sir Andrew Nobel) made numerous experiments in closed vessels with explosives, giving no solid products, such as guncotton, cordite and ballistite. Both cordite and ballistite are propellant agents for guns, and burn progressively, like gunpowder, without detonation, so that the crusher gauge readings indicate true pressures.

Sir Andrew Nobel's book, "Artillery and Explosives," made up of a series of essays and lectures, covering a period from 1858 to 1900, is the record of the life work of a celebrated artillerist and student of explosives. The book gives a resume of his great work in conjunction with Sir Frederick Abel, as well as his later investigation of smokeless powders.

On page 466 he gives a table of the pressures (tons on the square inch) for different densities of charge in closed vessels for four explosives—pebble gunpowder, amide powder, ballistite and cordite. The highest densities for the two latter are 0.26, the lowest 0.05. The highest pressures are 20.80 and 21.75 tons per square inch respectively. Now, if Boyle's law held rigidly, dividing the pressure by the corresponding density should give the pressure at unit density, and this should be the same throughout the table. Making a list of these quotients we find, in the case of cordite, for a density of 0.26, the pressure at unit density—83.6 tons, but this quotient declines by degrees in going down the list, till it reaches 60 tons for the density 0.05.

On page 426, a diagram of curves is given for the four explosives, showing the pressure at different densities—the maximum density given for cordite being about 0.615, for which the pressure is 65 tons. Deducing the pressure for unit density, we find it nearly 106 tons. On the preceding page the author states that he has measured pressures for this explosive up to 90 tons, and again, on page 469, he says that he has obtained pressures close upon 100 tons per square inch, but in neither case does he give the corresponding density. If, however, we extend the curve for cordite—page 426—keeping the curvature the same to unit density, we get about 142 tons, or 21,641 atmospheres.

If Boyle's law held exactly, the curve of pressures would be a straight line, and the pressure for unit density deduced from the pressure at any density would be a constant quantity. Part of the departure from the strict law is due to the greater relative loss of heat at the lower densities, for which the law would otherwise hold. Bichel, by eliminating the cooling effect, showed that Boyle's law held very exactly through a range of densities from $\frac{1}{150}$ to $\frac{1}{25}$. These densities, however, are very low. The range of the law is undoubtedly much more extended than this, and from his experiments on the products of gunpowder, the maximum pressure of which is well known, it appears probable that the law holds very approximately up to pressures of several thousand atmospheres, provided the influence of cooling be eliminated.

Suppose that we can calculate accurately the line of pressures for the dissociated products of an explosive, according to Boyle's law. This will show the pressures proportional to the densities being a right line through the origin of co-ordinates. Now, if the actual pressures be determined for different densities, up to, say, 0.6, and plotted on the same diagram, the curve beginning likewise at the origin, will fall below the line for the lower densities, and at a certain distance, corresponding, we will say, to 4000 atmospheres, it will cross the line and remain above it, becoming gradually steeper. The part below the straight line will be convex to the latter, which

will form a chord to the curve. If, on the other hand, we could eliminate the effect of the loss of heat at the lower densities, the curve would coincide with the straight line for these densities, but at a certain distance from the origin it would become a tangent and depart from it on its upward course.

To extend the actual curve for cordite to unit density, as suggested above, therefore gives too high a pressure, since its curvature is exaggerated by its crossing instead of being tangent to the line. The pressure of cordite at unit density is probably about 115 tons on the square inch. Assuming this to be accurate, it gives us a means of correcting the form of the curve, and its extension towards very high densities.

In considering the increase of pv under great pressures, it seems at first blush to be simply a question of density of the products, which is fixed by the capacity of the containing vessel, and the quantity of explosive used, without reference to the nature of its metamorphosis. If we compare equal volumes of hydrogen and of mercury vapour, at, say, 1000° C., we will find the pressures equal, but the latter will be 100 times as dense as the hydrogen. We can reason that the increase of pv *ceteris paribus* depends not upon the density, but the compression of the gases, and this for a given containing vessel will vary with the specific volume of the dissociated products of the explosive and the density of charge.

We have prepared the following table for the four explosives, nitro-glycerine, blasting gelatin, mercury fulminate and cordite, from the data available, and have plotted diagrams of the pressure curves, using the compressions (the maximum values are given in col. 6) as abscissas. The straight line, representing exact agreement with Boyle's law, being first drawn for each explosive, we have applied as tangent to it the extension of the corrected curve for cordite obtained from "Artillery and Explosives" (see page 426), and have obtained the pressures given in col. 8 for the maximum pressures of the dissociated products of the explosives.

Table—Pressures of Explosives—Dissociation and Deviation
of pv from Boyle's law taken into account.

	Explosive.	Spec. Vol. Final Products. C.C. per gramme.	Spec. Vol. Dissociated Pro- ducts. C.C. per gramme.	Pressure in Atmospheres Disso- ciated Products at Spec. Vol.	Pressure of Dissociated Pro- ducts at unit density of charge, Pv constant.	Maximum Density of Charge for Explosive.	No. Atms. of Compression Dis- sociated Products at Max. Density of Charge.	Pressure in Atms. at Max. Density of Explosive. Pv taken as constant.	Pressure at Max. Density, Allowing for Deviation of Pv from Boyle's Law.
	1	2	3	4 2×3	5	6 2×5	7 4×5	8	
Nitro-glycerine ..	713	914	12.50	11,425	1.60	1462	18,280	35,361	
Blasting Gelatin ..	710	917	12.80	11,737	1.63	1495	19,131	37,647	
Mercury Fulminate..	314.5	331.5	18.30	6,064	4.42	1465	26,777	49,155	
Cordite .. .	774	992	10.66	10,575	1.00	992	10,575	17,528	

It happens that the theoretical potential absolute pressures of the first three explosives on the list are approximately equal—being 30 to 32 thousand atmospheres. The reader will remember that these potential pressures are obtained by ignoring the effect of disassociation in diminishing the temperature and tension being calculated from the final products, and the heat of decomposition in accordance with the laws of gases. Now it will be noticed the absolute pressures of these explosives, given in the table (col. 8), exceed the potential pressures. This may strike the student as extraordinary, but though there is great uncertainty in our method of computation, we think there is no question about the fact, so far as all explosives, admitting of such great densities of charge, are concerned. The fulminate is apparently capable of reaching a pressure 60 per cent. higher than the potential. The uncertainties in the method of making these computations are many. In the first place, we have had to assume a pressure at unit density for cordite. This density corresponds to a compression of its products of 992 atmospheres. Then, we assume that the departure of pv from the

normal is the same for all the explosives at the corresponding compression—the deviation being independent of the nature of the gases. We next assume that the change of pv , when its departure from Boyle's law is once well established, is in accordance with a constant law—in other words, that the established curve, and its extension form the arc of a circle of great radius. This is possibly an error, as the deviation from successive tangents may be more rapid than this, but as this tendency may be counteracted by the effect of temperature (which is higher for the dissociated products of the fulminate than for the other explosives), I have thought it best to keep the radius of curvature constant.

CRITCHLEY



PARKER

PUBLICATIONS.

Coalfields and Collieries of Australia.

F. Danvers Power. 440 pages, 229 illustrations, demy octavo. 25/- nett.
Posted, 25/3; foreign, 26/8. (Size, 9 x 6.)

High Explosives.

W. R. Quinan. 224 pages, royal octavo, 21/- Posted,
21/3; foreign, 22/4. (Size, 10 x 7.)

Power.

Issued under authority Sydney Municipal Council.
2/6 nett; post free.

Australian Mining and Metallurgy.

Donald Clark. 600 pages, royal octavo. 21/- nett.
Posted, 21/4; foreign, 22/9. (Size 10 x 7.)

Metallurgy of Tin.

P. J. Thibault. 230 pages, demy octavo. 12/6 nett.
Posted, 12/8; foreign, 13/4. (Size, 9 x 6.)

Gold Refining.

Donald Clark. 134 pages (plates), demy octavo, 12/6
nett.
Posted, 12/7; foreign, 13/1. (Size, 9 x 6.)

West Australian Mining Industry.

Issued under the authority of the W.A. Government.
250 pages, crown folio. 10/- nett.
Posted, 10/2; foreign, 10/8. (Size, 14½ x 10.)

New South Wales Mines and Minerals.

250 pages, crown quarto. 5/- nett.
Posted, 5/1; foreign, 5/7. (Size, 10 x 7½.)

Victoria, and its Mining Resources.

Issued under the authority of the Victorian Government.
84 pages, crown quarto. 2/6 nett.
Posted, 2/7; foreign, 2/9. (Size, 10 x 7½.)

Mining and Railway Map of Australia.

(In preparation.) Cloth 21/-.

Electrical Progress in Australasia.

156 pages, royal quarto. 2/6.
Posted, 2/7; foreign, 2/11. (Size, 12 x 9½.)

Ventilation of Mines.

Johann Sarvaas. 60 pages. 2/7 post free. (Size,
9½ x 6½.)

Australasian Joint Stock Coy.'s Year Book.

R. L. Nash (Financial Editor, "Daily Telegraph,"
Sydney). 500 pages, demy octavo. 9/- nett. Posted,
9/2; foreign, 10/3. (Size, 9 x 6.)

Australian Mining Standard, Engineering and Electrical Record.

Issued every Thursday.

Weekly, 26/- per annum. Foreign, 30/- post free.
Size is stated in inches.

SYDNEY: 12-14 O'Connell-street.

MELBOURNE: 376 Flinders Lane.

LONDON: 22 Henrietta-street, Covent Garden, W.C.
and NEW YORK.

HIGH EXPLOSIVES.

By W. R. QUINAN.

With an Introductory Note by T. J. WRAMPELMEIER.

224 Pages, Royal 8vo. 21/- Nett.

This book was written while the author was in the last stages of a severe illness, to which he succumbed on August 15th, 1910, at Wahroonga, New South Wales. William Russell Quinan was born in Maryland, U.S.A., in 1848. He graduated from West Point, the Military Academy of the United States, in 1870, having distinguished himself for proficiency in mathematics and the physical science. After some years' service in the Artillery, he resigned his commission in 1881, to devote himself to the development and manufacture of industrial explosives. His first engagement was the California Vigorit Powder Company. From 1883 until 1889, he was Superintendent of the California Powder Works. In 1889, he was engaged by the late Cecil Rhodes to build a dynamite factory in South Africa, and was appointed General Manager of the Cape Explosives Works Limited. He remained with this company until the end, and it was while in Australia in its interest that the last illness overtook him. He was a prolific inventor, amongst his novelties being the first successful machine for packing dynamite into cartridges, and a crusher gauge for the testing of high explosives.

COALFIELDS AND COLLIERIES OF AUSTRALIA.

By F. DANVERS POWER.

440 Pages. 229 Illustrations. Demy 8vo. 25/- Nett.

The author deals exhaustively with the subject, not merely from a geological point of view, but mainly with the actual working of collieries in the various States of the Commonwealth. The methods of mining employed in different localities and by the different companies in one locality; the surface and underground machinery and plant; electrical equipments, coal-cutters, air-compressors, and the latest devices adopted to make operations profitable as well as safe; the railway and trolley-track schemes, with detailed descriptions of rolling stock, are fully described. The great collieries of New South Wales naturally furnish the larger amount of the contents, but those of the other States are made to contribute to the completeness of the work. The illustrations include diagrams and photographs of machinery; railways, surface and underground; coking ovens and their plant; and everything of which a more graphic idea is required than can be given in words.

AUSTRALIAN MINING AND METALLURGY.

By DONALD CLARK, B.C.E., M.M.E.

600 Pages. Royal 8vo. 21/- Nett.

The author's wide experience and his eminence in his profession rendered him specially fitted for the work of describing "Australian Mining and Metallurgy"—the multifarious methods employed in the most important mines of each State for the reduction of ores, and the recovery of their metallic contents, be they Gold, Silver, Lead, Tin, Zinc, or what not. Descriptions of the principal mines—gold, silver, copper, tin, etc.—in Australasia; characteristic geological formations, the methods of working the deposits, peculiarities of treatment according to the nature of the ores—their simplicity, complexity, refractoriness; concentration, sintering, precipitation; chlorination and cyanidation; roasting, retorting, refining; the different patent processes which experience has proved to be most suitable in various circumstances, are lucidly explained. Metallurgical hints are scattered throughout the book, and a special section is devoted to that part of the subject which will prove of great value.

AUSTRALIAN MINING STANDARD, ENGINEERING AND ELECTRICAL RECORD.

Per copy, 6d. Annual subscription in Australasia, 26s.; Abroad, 30s.

This is something more than the leading Australian mining and engineering weekly: it is the only one. It caters for the mining investor, the mine manager, the metallurgist, the geologist, the mineralogist, and every species of engineer. No one who wishes to keep pace with the developments in Australian mining or with the developments in mining and engineering practice can afford to be without it. The very latest London quotations for the principal metals are cabled for each issue; and, by means of a competent staff of local correspondents, readers of the paper are kept au fait with the work done on all the leading fields of Australia. The stocks attracting most attention on 'Change are dealt with by a writer specially qualified for the task, and electrical and mechanical engineers find technical articles of the highest value to them in the shape of monographs written specially for the paper, and summaries of contributions made to the proceedings of leading English and Continental scientific societies, furnished by an exceedingly capable London correspondent. A space is also reserved for financial matters, and Australian trade returns are published.

GOLD REFINING.

By DONALD CLARK, M.M.E.

134 Pages Demy 8vo. Illustrated. 12/6 Nett.

"To present the essential points of all methods of gold refining commonly practised, as well as those of historic interest," was the author's purpose in this volume. The fifteen chapters of which the book consists deal with the Simpler Methods of Early Days; Amalgamation Process; Refining with Oxidising and Chloridising Agents; Sulphur Refining; Refining with Cementation Processes, and by means of Oxygen and Air; Miller's Process and that adopted at the Melbourne Mint; Parting with Nitric Acid (two chapters); Recovery of Silver from Nitrate Solutions; Refining by Sulphuric Acid; Parting by Electrolysis; Electrolytic Refining of Gold; Separation of Platinum from Gold; Treatment of Cyanide Precipitates; Refining of Gold Slimes by Nitric and Sulphuric Acid; the Nitre Cake Method of Purifying Slimes.

THE AUSTRALASIAN JOINT STOCK COMPANIES' YEAR-BOOK.

By ROBERT LUCAS NASH,

Financial Editor of Sydney "Daily Telegraph,"
Author of "Investor's Sinking Fund and Redemption Tables," "Profitable Nature of Our Investments," Eight Editions of
"Fenn on the Funds" (London), etc.

500 Pages, Demy 8vo. 1912 Edition. Price, 9/- Nett.

A Complete Official Record of all Australasian Investments—including Government and Municipal Loans, Railways and Tramways, Banking, Insurance, Gas and Water, Shipping, Mortgage and Financial, Land and Pastoral, Investment, Brewery, Trading, Manufacturing, and other Companies; as well as Mining Companies of all descriptions—to which both Australasian and British Capital has been subscribed.

ELECTRICAL PROGRESS IN AUSTRALASIA.

156 Pages. Royal 4to. 2/6 Nett.

The wonderful progress of the applications of electricity to modern life and industry in Australasia during the past few years has hitherto been indicated in scattered pages of newspapers and isolated articles in magazines; there has been no attempt to collect the details of electrical development into one body, at all times easy of access and reference. That want is supplied in these pages. All the most representative installations, for whatever purpose—lighting, power, haulage, or metallurgical work, are here described at length by experts. The more or less complete systems of electric tramways of the several States; the ever-increasing demands for electric lighting, which come now-a-days from every moderately prosperous country township; the application of electricity to various purposes in mining operations and in factories, are duly recorded. Anyone wishing to know how much has been done in utilising electrical power throughout Australia will find no other book so comprehensive in scope as this.

Second Edition will be edited by W. G. T. Goodman, Engineer-in-Chief
Tramway Trust, Adelaide, S.A.

MINING AND RAILWAY MAP OF AUSTRALIA.

Mounted and Varnished for Wall; price, 21/-.

Up to the present time there is not in existence any Map of Australia which gives on a single sheet the whole of the Mineral Fields of the Continent, nor even one showing the whole of the Railways, whether in actual being or in course of construction. The task of combining the whole of these, and of adding such new mineral Fields as have since been opened up and such Railway extensions as the growing trade of the Commonwealth has necessitated, has been entrusted to experts in Cartography. All those who are financially interested in mining will recognise the importance of knowing how far a particular field is from railway communication; and the same consideration is a factor in the Commercial value of Agricultural and Timber areas, so that this publication will be of great value to the Commercial Community generally.

VICTORIA AND ITS MINING RESOURCES.

ISSUED UNDER AUTHORITY, VICTORIAN GOVERNMENT.

84 Pages, Crown 4to. 2/6 Nett.

After an introduction covering the early years of the colony, and contrasting the conditions of things then with those of to-day, the author deals succinctly with the history, development, characteristics, and productiveness of the several goldfields to which, to so large an extent, the progress of Victoria is attributable. The book is by no means technical; it is a pleasantly-written and reliable summary of what has been done, together with so much of geological information as was necessary to convey a full impression. Special chapters are devoted to deep leads mining, dredging for gold, nuggets, coal, economic minerals, and timber resources.

WEST AUSTRALIAN MINING INDUSTRY.

ISSUED UNDER AUTHORITY, W.A. GOVERNMENT.

250 Pages, Cream Folio, with Maps, Plans, and Numerous Illustrations. 10/-

The suddenness with which the Golden West came to the fore as a gold-producer, and its continued productiveness in spite of many fluctuations of fortune, lend an air of romance to any description of its mining pursuits. But beneath the romance is a substratum of substantial production, and this book gives a broad, general idea of the steady progress of Western Australia from the days when Kalgoorlie and Coolgardie, Yilgarn, Phillips River, and Murchison were unknown localities in a barren desert, to the time when they had become flourishing centres of industry. While gold has been the principal creator of all this prosperity, mining for other products is not overlooked in these pages, and the general reader, as well as the practical miner, will find it a storehouse of information.

THE "MINING STANDARD" AND MINING MEN.

It gives me pleasure to congratulate you upon the advance you have made, not only in its production, but also in the valuable matter it contains.—F. M. DICKENSON.

The paper has always taken a reasonable stand, but, at the same time, a strong one.—G. H. BLAKEMORE.

Your paper has always taken a leading place in disseminating useful information relating to the mining industry.—JAMES PARK, N.Z.

All credit is due to you for the manner in which you have overcome the many difficulties you must have encountered in soundly establishing a technical paper.—H. H. SCHLAPP.

Its sound advocacy of mining on straight financial lines and scientific methods speaks volumes for both management and staff.—V. J. SADDLER.

I have to express my appreciation of the many excellent technical papers which, for some time past, have been appearing in your columns.—STANLEY LOW.

I am a constant reader of the "Standard," and in it have found much of interest and value in my work.—J. W. BELL, Director Geological Survey, N.Z.

I trust you will, in the future, pursue the publication of useful technical books. . . . Those that have issued from your press from time to time have, I am certain, been highly appreciated.—ROBT. STICHT.

The paper has, to my knowledge, been run upon sound and clean lines throughout, and done much for the mining industry in Australia.—HON. WM. KNOX.

You are to be congratulated upon the fact that you have been able, with the handful of scientific writers available in Australia, to maintain the interest of your readers on technical matters.—E. A. WEINBERG.

It has given me pleasure to notice that you have always run the "Mining Standard" on fearless lines, regardless of friend and foe.—BOWES KELLY.

It has always been carried on in a way which stamps it of real value, not only to the investor, but to the mine manager as well.—WM. JAMIESON.

UNIVERSITY OF CALIFORNIA LIBRARY

This book is DUE on the last date stamped below.

Fine schedule: 25 cents on first day overdue

50 cents on fourth day overdue

One dollar on seventh day overdue.

DEC 1 1947

LD 21-100m-12, '46 (A2012s16) 4120

TP270
Q7
Mining
Dept

256532

Dunnand

